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Fibrillated polyolefin material - contains fibrils having a set dia. and are orientated in one direction and has high strength, good adhesivity and flexibility
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Polyolefin material is fibrillated and the fibrils have a dia. of 0.1-50 microns and are oriented in one direction.

To prepare the material, polyolefin having super-high mol. wt. is rolled and/or drawn. Then it is treated with ultrasonic wave. The polyolefin to be used is pref. a homo- or co-polymer of (alpha)olefin having 2-12C, pref. 2-8C (in copolymerisation, olefins having different numbers of carbon atom are used). The mol. wt. is pref. 0.9-9 million. The ultrasonic wave treatment is carried out in water pref. with 20-200 kHz wave of 10-50 kW/100 ml water at 20-65 deg.C for 10-60 min.

USE/ADVANTAGE - A sheet of this polyolefin has a tensile strength as high as 1-2.5 GPa. Polyolefin materials of high strength have already been known, but the material proposed here is better in flexibility and adhesiveness to other polymer materials.

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【文献】特開　昭６０－１７３１５５（ＪＰ，Ａ）	[Reference] Japan Unexamined Patent Publication Showa 60-1731 55 (JP,A)
【文献】特開　昭６０－１０１０３２（ＪＰ，Ａ）	[Reference] Japan Unexamined Patent Publication Showa 60- 10 1 0 32 (JP,A)
(57)【特許請求の範囲】	(57) [Claim(s)]
【請求項１】超高分子量ポリオレフィンを圧延および／または延伸したのち、超音波処理して同一方向に直径0.１～５０μｍのフィブリル構造を生ぜしめることを特徴とするフィブリル化ポリオレフィン材料の製造方法。	[Claim 1] Ultrahigh molecular weight polyolefin after rolling and d rawing,　ultrasonic treatment doing, it designates that it causes fibril structure of diameter 0.1 to 50 μmin same direction as feature, production method　of　fibrillated polyolefin material.
【請求項２】圧延および／または延伸が溶媒に溶解させる	[Claim 2] Production method　which designates that it is done in s

ことなくまた溶融工程を経ることのない固相状態において行われることを特徴とする特許請求の範囲第1項記載の製造方法。

olid phase state which therolling or / or drawing, does not melt in solvent, in addition doesnot pass melt step as feature, states in Claim 1 of patent claim.

【発明の詳細な説明】〔産業上の利用分野〕

[Description of the Invention] (Industrial Area of Application)

本発明はフィブリル化ポリオレフィン材料の製造方法に関し、詳細には、高強度でかつ柔軟性を有し、しかも他材料との積層化が容易なフィブリル化ポリオレフィン材料の製造方法に関する。

This invention regards production method of fibrillated polyolefi n material. In detail, it possesses and flexibility with high strength, furthermore itregards production method of fibrillated polyolefin material where lamination of other material iseasy.

〔従来技術および発明の解決しようとする課題〕

Problem which (the conventional technology and invention it tri es to solve.]

超高分子量ポリオレフィンをシートまたはテープに成形しこれを延伸することにより、高強度・高弾性率ポリオレフィン材料が得られることが知られている。例えば、特開昭59−130313号公報には、超高分子量ポリエチレンとワックスを溶融混合しこの混練物を押出し、冷却固化後、延伸することが記載されている。また、特開昭60−101032号公報には、超高分子量ポリエチレン溶液を冷却して得られるゲル状物を圧縮成形し、次いで延伸することが記載されている。さらに、特開昭63−66207号公報には、超高分子量ポリエチレンを融点以下の温度で圧縮成形し、しかる後圧延成形し延伸する方法が記載されている。

Ultrahigh molecular weight polyolefin it forms in sheet or tape, i t is informed that high strengthhigh modulus polyolefin material isobtained drawing this by doing. ultrahigh molecular weight polyethylene and wax melting and mixing are done in for example Japan Unexamined Patent Publication Showa 59-1303 13 disclosure, this kneaded substancethe extrusion is done, after cooling and solidification, what drawing is done is stated. In addition, in Japan Unexamined Patent Publication Showa 60- 10 10 3 2 disclosure, cooling ultrahigh molecular weight polyethylene solution, compression molding it does thegelled product which can. What drawing is done next is stated. Furthermore, ultrahigh molecular weight polyethylene compression molding is done to Japan Unexamined Patent Publication Showa 63-6620 7 disclosure, with temperatureof melting point or lower. after that rolling it forms and method which drawingis done is stated.

これらの方法で得られる超高分子量ポリエチレンシート、テープまたは繊維等の材料は軽量でかつ高強度で耐水性に優れていることから、これらを撚り合わせて海洋ロープにしたり、製織してオープンクロスとし、防爆シート等の用途に供されている。

Material of ultrahigh molecular weight polyethylene sheet , tape o r fiber etc which is obtained with these method, withthe light weight and from fact that in high strength it is superior in thewater resistance, these twist making weaving doing together ocean rope, itmakes open cloth, is offered to application of explosion proofing sheet etc.

しかしながら、これらのロープあるいはオープンクロスは、高強度であるが、同時に弾性率が高いために柔軟性に欠けるという難点があった。

But, these rope or open cloth are high strength, but there was a d ifficultythat because elastic modulus is high in same time, is lacked in flexibility.

また、これらの延伸シートまたはテープにマトリックス用樹脂を積層し積層体とする場合、あるいは他の材料と複合化を図る場合、樹脂あるいは他材料との接触面積が限られているために、充分な接着強度が得られないという問題点があった。

In addition, when laminated layer does resin for matrix in thesedr awing sheet or tape and makes laminate, or when composite making is assured with other material, there was a problem that because contact area of resin or other materialis limited, you cannot obtain satisfactory adhesion strength.

〔課題を解決するための手段〕

(means in order to solve problem)

上記の問題点を解決すべく鋭意検討した結果、特定のポリオレフィンを圧延および／または延伸したのち、超音波処理することにより、有用なフィブリル化ポリオレフィン材料が得られることを見出し、特にかかるフィブリル化ポリオレフィン材料が高強度でかつ柔軟性を有し、他材料との接着性に優れる等の特徴を有することを見出して、本発明に到達したものである。

In order that above-mentioned problem is solved, diligent investi gation it did. Fact that useful fibrillated polyolefin material is obtained specific polyolefin afterthe rolling and drawing, by ultrasonic treatment doing, was discovered. Especially fibrillated polyolefin material being high strength, and it possesses flexibility, suchas is superior in adhesiveness of other material discovering factthat it possesses feature, it is something which arrives in this invention.

すなわち、本発明は、超高分子量ポリオレフィンを圧延および／または延伸したのち、超音波処理することを特徴とする同一方向に直径0.1～50μmのフィブリル構造を生ぜしめることを特徴とするフィブリル化ポリオレフィン材料の製造方法に関する。

以下、本発明についてさらに詳細に説明する。

本発明におけるフィブリル化ポリオレフィン材料は、直径0.1～50μm、好ましくは、0.5～30μm、さらに好ましくは、1～20μmのフィブリルを同一方向に配列しているものである。かかる配列方向は、通常、ポリオレフィン材料を製造する際の圧延または延伸方向と同一である。

本発明のフィブリル化ポリオレフィン材料は、超高分子量のポリオレフィンを圧延および／または延伸したのち、超音波処理することにより、容易に製造される。以下、製造工程について詳述する。

1）超高分子量ポリオレフィン

本発明で用いる超高分子量ポリオレフィンとしては、炭素数2～12、好ましくは、2～8のα－オレフィンの単独重合体、例えば、ポリエチレン、ポリプロピレン、ポリブテン－1等、あるいは互いに炭素数の異なるα－オレフィン同士の2元以上の共重合体、例えば、エチレンと炭素数3～12、好ましくは3～8のα－オレフィン（例えば、プロピレン、ブテン－1、4－メチルペンテン－1、ヘキセン－1等）との共重合体（α－オレフィン含量は、通常、10モル%以下、好ましくは0.01～5モル%）、プロピレンと炭素数4～12のα－オレフィンとの共重合体等が例示できる。また、コモノマーとして、ジエン類、例えばブタジエン、1,4ヘキサジエン、ビニルノルボルネン等をさらに併用して得られる共重合体等も例示できる。

本発明の超高分子量ポリオレフィンは、通常、分子量が50万～1200万、好ましくは、90万～900万であり、例えば、ポリエチレンまたはエチレン・α－オレフィン共重合体の場合、粘度平均分子量が50万～1200万、好ましくは、90万～900万、さらに好ましくは120万～600万の範囲であり、135℃デカリン中における極限粘度により表記すれば、5～50dl/g、好ましくは8～40dl/g, さらに好ましくは10～30dl/gであるいわゆる超高分子量ポリエチレンであることが好ましい。

ポリオレフィンの分子量が50万より小さいと延伸物または圧延物の機械的物性が悪くなる場合があり、また、1200万を越えると圧縮成形、圧延および延伸を行う場合の加工性が悪くなる場合がある。

Namely, this invention, ultrahigh molecular weight polyolefin af ter rolling and drawing, designates thatthe ultrasonic treatment it does as feature, it designates that fibril structure of diameter 0.1 to 50 μm is caused in same direction asfeature, it regards production method of fibrillated polyolefin material.

Furthermore you explain in detail concerning below and this inv ention.

Fibrillated polyolefin material in this invention, diameter 0.1 to 50 μm , preferably, and 0.5 to 30 μm ,furthermore is something which arranges fibril of preferably, and the1 to 20 μm into same direction. This arrayed direction, usually, case where polyolefin material is produced, isidentical with rolling or drawing direction.

Fibrillated polyolefin material of this invention is produced easily polyolefin of ultrahigh molecular weight afterthe rolling and drawing, by ultrasonic treatment doing. You detail concerning below and production step.

1) ultrahigh molecular weight polyolefin

As ultrahigh molecular weight polyolefin which is used with this i nvention, homopolymer of carbon number 2 to 12, the preferably, and 2 to 8 α-olefin. for example , polyethylene , polypropylene and polybutene -1 etc. Or copolymer above 2 dimensional of α-olefin where carbon number differsmutually. α-olefin of for example , ethylene and carbon number 3 to 12 and preferably, 3 to 8 (Such as for example , propylene , butene -1, 4-methylpentene -1 and hexene -1) with copolymer (α-olefin content usually, 10 mole % or less and preferably, 0.01 to 5 mole %). copolymer etc of propylene and carbon number 4 to 12 α-olefin. It can illustrate. In addition, furthermore dienes , for example butadiene , 1,4 hexadiene and vinyl norbornene etc as comonomer, it can illustrate also copolymer etcwhich can obtain by jointly using .

As for ultrahigh molecular weight polyolefin of this invention, us ually, molecular weight is 500,000to 12000,000,the preferably, and 900,000to 9000,000. for example , polyethylene or ethyleneα-olefin copolymer in case, viscosity average molecular weight 500,000to 12000,000,the preferably, and 900, 000to 9000,000, furthermore is range of thepreferably, 1200, 000to 6000,000. If you inscribe with limiting viscosity in in 135 °C decalin, it is desirable the5 to 50 dl/g and preferably, 8 to 40 dl/g , furthermore to be a preferably, 10 to 30 dl/g, to be a so-called ultrahigh molecular weight polyethylene.

When molecular weight of polyolefin is smaller than 500,000, th ere are timeswhen mechanical property of drawn article or rolled article becomes bad. In addition, when it exceeds 12000,000, there are times when fabricabilitywhen compression molding , rolling and drawing are done becomes bad.

また、これらの超高分子量ポリオレフィンの形状は特に限定されないが、通常、顆粒状、粉末状のものが好ましく用いられ、例えば粒径が2000μm以下、好ましくは1～2000μm、さらに好ましくは10～1000μmが望ましい。また、その粒径分布は狭い方が圧縮成形時において欠陥部が少なく、均質なシート、フィルム状物が得られる点で好ましい。

In addition, shape of these ultrahigh molecular weight polyolefin especially is not limited, butusually, granule and powder are desirable using. for example grain size 2000 μm or less and preferably, 1 to 2000 μm, furthermore preferably, 10 to 10 00 μm is desirable. In addition, as for particle diameter distribution narrower one, defective part is little in thetime of compression molding, is desirable in point where you can obtain the uniform sheet and film.

本発明で使用される上記の性状を有する超高分子量ポリオレフィンは、周期律表IV～VI族の遷移金属元素を含む化合物のうち、少なくとも一種の化合物を含有する触媒成分と、必要に応じて有機金属化合物とを組合わせてなる触媒の存在下に、α－オレフィンを重合または共重合することにより得られる。

As for ultrahigh molecular weight polyolefin which possesses above-mentioned properties which isused with this invention, among compound which include transition metal element of the Periodic Table IV to Group VI, under presence of catalyst which becomes combining catalyst component which at least contains compound of one kind, according to need organometallic compound, It is obtained α-olefin polymerization or by copolymerization doing.

触媒成分を構成するところの周期律表IV～VI族の遷移金属を含む化合物としては、具体的にはチタン化合物、バナジウム化合物、クロム化合物、ジルコニウム化合物、ハフニウム化合物等が好適である。また、これらの化合物を複数種組合わせて用いてもよい。

As compound which includes transition metal of Periodic Table IV to Group VI which forms thecatalyst component, titanium compound, vanadium compound, chromium compound, zirconium compound and hafnium compound etc are idealconcretely. In addition, multiple kinds combining these compound, it is possible to use.

チタン化合物としては、チタンのハロゲン化物、アルコキシハロゲン化物、アルコキシド、ハロゲン化酸化物等を挙げることができ、４価のチタン化合物と３価のチタン化合物が好適である。４価のチタン化合物としては具体的には一般式

As titanium compound, halide of titanium, to be able list alkoxy halide, the alkoxide and oxyhalide etc. titanium compound of quaternary titanium compound and trivalent is ideal. Concrete as quaternary titanium compound general formula

$Ti(OR)_nX_{4-n}$

（ここでRは炭素数１～20好ましくは１～12のアルキル基、またはアラルキル基を示し、Xはハロゲン原子を示す。nは$0 \leqq n \leqq 4$である。）で示されるものを挙げることができ、特に四塩化チタンが好ましい。

$Ti(OR)_nX_{4-n}$

It can list those which are shown with (Here as for R alkyl group, or aralkyl group of carbon number 1 to 20 preferably, 1 to 12 showing. X shows halogen atom. n is $0 \leq n \leq 4$.), especially titanium tetrachloride isdesirable.

３価のチタン化合物としては三塩化チタン等の三ハロゲン化チタンが挙げられ、また、一般式

Be able to list titanium trihalide of titanium trichloride etc as titanium compound of trivalent,in addition, general formula

$Ti(OR)_mX_{4-m}$

（ここでRは炭素数１～20のアルキル基、アリール基またはアルキル基を示し、Xはハロゲン原子を示す。mは$0 \leqq m \leqq 4$である。）で示される４価のハロゲン化アルコキシチタンを周期律表Ｉ～III族金属の有機金属化合物により還元して得られる３価のチタン化合物が挙げられる。

$Ti(OR)_mX_{4-m}$

quaternary alkoxy titanium halide which is shown with (Here as for R alkyl group of carbon number 1 to 20, aryl group or alkyl group showing. X shows halogen atom. m is $0 \leq m \leq 4$.), with organometallic compound of Periodic Table I to Group III metal, you can list titanium compound of trivalent which can obtain by reduction doing.

これらのチタン化合物のうち、４価のチタン化合物が特に好ましい。

Among these titanium compound, quaternary titanium compound especially is desirable.

バナジウム化合物としては、バナジウムのハロゲン化物、アルコキシハロゲン化物、アルコキシド、ハロゲン化酸化物を挙げることができ、具体的には、四塩化バナジウム等の四ハロゲン化バナジウム、テトラエトキシバナジウムの如く４価のバナジウム化合物、オキシ三塩化バナジウム、エトキシジクロルバナジル、トリエトキシバナジル、ト

As vanadium compound, halide of vanadium, to be able list alkoxy halide, the alkoxide and oxyhalide. Concrete, four halogenation vanadium of vanadium tetrachloride etc. quaternary vanadium compound like tetra ethoxy vanadium. vanadium compound of pentavalent like vanadium oxytrichloride, ethoxy dichlor vanadyl, triethoxy vanadyl and the tributoxy vanadyl.

リブトキシバナジルの如き５価のバナジウム化合物、三塩化バナジウム、バナジウムトリエトキシドの如き３価のバナジウム化合物が挙げられる。

You can list vanadium compound of trivalent like vanadium trichloride and vanadium triethoxide.

さらに上記チタン化合物またはバナジウム化合物を１種以上の電子供与性化合物で処理してもよい。電子供与性化合物としては、エーテル、チオエーテル、チオールホスフィン、スチビン、アルシン、アミン、アミド、ケトン、エステル等を挙げることができる。

Furthermore it is possible to treat above-mentioned titanium com pound or thevanadium compound with electron donating compound above 1 kind. As electron donating compound, it can list ether , thioether , thiol phosphine , stibine ,the arsine , amine , amide , ketone and ester etc.

また、チタン化合物またはバナジウム化合物はマグネシウム化合物と併用してもよい。併用されるマグネシウム化合物としては、金属マグネシウム、水酸化マグネシウム、炭酸マグネシウム、酸化マグネシウム、フッ化マグネシウム、塩化マグネシウム、臭化マグネシウム、ヨウ化マグネシウム等、また、ケイ素、アルミニウム、カルシウムから選ばれる金属とマグネシウム原子とを含有する複塩、複酸化物、炭酸塩、塩化物あるいは水酸化物等、さらにはこれらの無機質固体化合物を含酸素化合物、含硫黄化合物、芳香族炭化水素、ハロゲン含有物質で処理または反応させたもの、また、ケイ素、アルミニウムを含有する酸化物に、上記のマグネシウム化合物を含有させたもの等が挙げられる。

In addition, it is possible to jointly use titanium compound or va nadium compound,with magnesium compound. As magnesium compound which is jointly used, metal magnesium , magnesium hydroxide , magnesium carbonate ,the magnesium oxide , magnesium fluoride , magnesium chloride , magnesium bromide and magnesium iodide etc. In addition, double salt which contains with metal and magnesium atomwhich are chosen from silicon , aluminum , calcium. compound oxide , carbonic acid salt , chloride or hydroxide etc. Furthermore these inorganic substance solid compound those which with oxygen containing compound , sulfur containing compound , aromatic hydrocarbon , halogen-containing substance it treats or react,or. In addition, in oxide which contains silicon , aluminum, those whichcontain above-mentioned magnesium compound. Such as is listed.

チタン化合物またはバナジウム化合物とマグネシウム化合物を併用する場合、両者の接触方法としては、特に制限はなく、公知の方法を採用することができる。

When titanium compound or vanadium compound and magnesium compound are jointly used, there isnot especially restriction as contact method of both, can adopt the known method.

上記の含酸素化合物としては、例えば水、アルコール、フェノール、ケトン、アルデヒド、カルボン酸、エステル、ポリシロキサン、酸アミド等の有機含酸素化合物、金属アルコキシド、金属のオキシ塩化物等の無機含酸素化合物を例示することができる。含硫黄化合物としては、チオール、チオエーテルの如き有機含硫黄化合物、二酸化硫黄、三酸化硫黄、硫酸の如き無機硫黄化合物を例示することができる。芳香族炭化水素としては、ベンゼン、トルエン、キシレン、アントラセン、フェナンスレンの如き各種単環および多環の芳香族炭化水素化合物を例示することができる。ハロゲン含有物質としては、塩素、塩化水素、金属塩化物、有機ハロゲン化物の如き化合物等を例示することができる。

As above-mentioned oxygen containing compound, for example water, organic oxygen containing compound of alcohol ,the phenol , ketone , aldehyde , carboxylic acid , ester , polysiloxane andthe acid amide etc. inorganic oxygen containing compound of metal alkoxide and oxy chloride etc of metal can beillustrated. As sulfur containing compound, organic sulfur containing compound like thiol , thioether. inorganic sulfur compound like sulfur dioxide , sulfur trioxide , sulfuric acid. It can illustrate. As aromatic hydrocarbon, various monocycle and polycyclic aromatic hydrocarbon compound like benzene , toluene , xylene , the anthracene and phenanthrene can be illustrated. As halogen-containing substance, chlorine , hydrogen chloride , metal chloride and compound etc likethe organic halide can be illustrated.

他の触媒系の例としては、いわゆるグリニヤ化合物等の有機マグネシウム化合物とチタン化合物との反応生成物を用い、これに有機アルミニウム化合物を組合わせた触媒系を例示することができる。

As example of other catalyst system, reaction product of organo magnesium compound and titanium compound ofthe so-called Grignard compound etc is used. catalyst system which combines organo-aluminum compound to this can be illustrated.

また他の触媒系の例としては、SiO_2, Al_2O_3等の無機酸化物と前記少なくともマグネシウムおよびチタンを含有する固体触媒成分を接触させて得られる固体物質を用い、これに有機アルミニウム化合物を組合わせたものを例示することができる。

In addition as example of other catalyst system, inorganic oxide of SiO_2, Al_2O_3 etc, description above solid catalyst component which at least contains magnesium and thetitanium, contacting, it uses solid substance which can obtain . Combination organoaluminum compound to this can be illustrated.

これらの触媒系において、チタン化合物を有機カルボン

In these catalyst system, with titanium compound as adduct of or

酸エステルとの付加物として使用することもでき、また前記したマグネシウムを含む無機固体化合物を有機カルボン酸エステルと接触処理させたのち使用することもできる。また、有機アルミニウム化合物を有機カルボン酸エステルとの付加物として使用しても何ら支障がない。さらには、あらゆる場合において、有機カルボン酸エステルの存在下に調整された触媒系を使用することも何ら支障なく実施できる。

クロム化合物としては、具体的には三酸化クロムまたは焼成によって少なくとも部分的に酸化クロムを形成する化合物を無機酸化物担体に担持させたフィリップス触媒と称される触媒を挙げることができる。無機酸化物担体としては、シリカ、アルミナ、シリカーアルミナ、チタニア、ジルコニア、トリアあるいはこれらの混合物が挙げられるが、シリカ、シリカーアルミナが好ましい。

担持するクロム化合物としてはクロムの酸化物、または焼成によって少なくとも部分的に酸化クロムを形成する化合物、例えばクロムのハロゲン化物、オキシハロゲン化物、硝酸塩、酢酸塩、硫酸塩、アルコラート等が挙げられ、具体的には三酸化クロム、塩化クロミル、重クロム酸カリウム、クロム酸アンモニウム、硝酸クロム、酢酸クロム、クロムアセチルアセトネート、ジターシャリブチルクロメート等が挙げられる。

担体にクロム化合物を担持させる方法としては、含浸、溶媒留去、昇華等の公知の方法によって行うことができ、使用するクロム化合物の種類によって適当な方法を用いればよい。担持するクロムの量は、担体に対するクロム原子の重量%で0.1～10重量%、好ましくは0.3～５重量%、さらに好ましくは0.5～３重量%である。

以上のようにしてクロム化合物を担持した担体を焼成して活性化を行う。焼成活性化は一般に水分を実質的に含まない非還元性雰囲気、例えば酸素存在下に行われるが、不活性ガスの存在下あるいは減圧下で行ってもよい。好ましくは乾燥空気が用いられる。焼成は、温度450℃以上、好ましくは500～900℃で数分～数時間、好ましくは0.5～10時間行う。焼成時は充分に乾燥空気を用い、流動状態下で活性化を行うのが好ましい。

なお、担持もしくは焼成時にチタネート類やフッ素含有塩類等を添加して、活性等を調節する公知の方法を併用してもよい。

また、このクロム化合物を担持した触媒を一酸化炭素、エチレン、有機アルミニウム等で還元して用いてもよい。

ジルコニウム化合物またはハフニウム化合物としては、例えば共役π電子を有する基を配位子としたジルコニウム化合物またはハフニウム化合物等が挙げられ、一般式、

ganic carboxylic acid ester, to be ablealso use. In addition before organic carboxylic acid ester and contact process after doing, also can theinorganic solid compound which includes magnesium which was inscribed use. In addition, using organo-aluminum compound as adduct of organic carboxylic acid ester, there is not ahindrance. Furthermore, in in case of all, under existing of organic carboxylic acid ester, it canexecute using catalyst system which was adjusted without hindrance.

As chromium compound, concrete chromium trioxide , or comp ound which at least forms partially chromium oxide with sintering, thebearing is done to inorganic oxide carrier , is possible fact that catalyst which is named Philips catalyst which is listed . As inorganic oxide carrier, silica , alumina , silica-alumina , titania , zirconia and thoria or you can list these mixture, but. silica and silica-alumina are desirable.

As chromium compound which bearing is done oxide of chromiu m, or compound which at least forms partially chromium oxide with sintering. halide of for example chromium, listing oxyhalide , nitrate salt , acetate , sulfate and alcoholate etc. You can list chromium trioxide , chromyl chloride , potassium dichromate , ammonium chromate , chromium nitrate ,the chromium acetate , chromium acetylacetonate and di tertiary butyl chromate etc concretely.

as method which bearing is done chromium compound in carrier, it to be possible to do with known method of impregnation , solvent removal and the sublimation etc. suitable method should have been used with types of chromium compound which youuse. Quantity of chromium which bearing is done, 0.1 to 10 wt% and the preferably, 0.3 to 5 wt% , furthermore is preferably, 0.5 to 3 wt% with wt% of chromium atom for the carrier.

Sintering doing carrier which chromium compound bearing is done likeabove, it does activation. As for sintering activation nonreducing atmosphere which does not include water in theactual generally. Under for example oxygen existing it is done, but. It is possible to do under existing of inert gas or under reduced pressure. It can use preferably, dry air. several minutes to several time, preferably, 0.5 to 10 hours it does sintering, with temperature 450 °C or higher and preferably, 500 to 900 °C. At time of sintering it is desirable in satisfactory to do activationunder flowing state, making use of dry air.

Furthermore, adding titanate and fluorine containing salts etc at t ime of the bearing or baking, it is possible to jointly use known method whichadjusts activity etc.

In addition, doing catalyst which this chromium compound bearin g is done, reductionwith such as carbon monoxide , ethylene and organoaluminum it is possible to use.

As zirconium compound or hafnium compound, be able to list zirc onium compound or hafnium compound etc whichdesignates group which possesses for example conjugated π electron as ligand, the

$R^1{}_aR^2{}_bMR^3{}_cR^4{}_d$

（ここで、Mはジルコニウムまたはハフニウム原子を示し、R^1, R^2, R^3およびR^4は炭素数１～20の炭化水素残基、ハロゲン原子または水素原子を示す。なお、R^1, R^2, R^3, R^4のうち少なくとも一つは炭化水素残基である。a, b, cおよびdはa＋b＋c＋d＝４なる条件式を満たすものである）で表わされる化合物が具体的に挙げられる。式中の炭化水素残基としてはアルキル基、アリール基、シクロアルキル基、アラルキル基、アルコキシ基、シクロアルカジエニル基、含硫黄炭化水素残基、含窒素炭化水素残基または含リン炭化水素残基等であることが好ましい。

general formula ,

$R^1{}_aR^2{}_bMR^3{}_cR^4{}_d$

You can list compound which is displayed with (Here, as for M zirconium or hafnium atom showing. R^1,R^2,R^3 and R^4 show carbon number 1 to 20 hydrocarbon residue , halogen atom or hydrogen atom. Furthermore, inside at least one of R^1,R^2,R^3,R^4 is hydrocarbon residue. a,b,c and d are something which fills up condition whichbecomes a+b+c+d=4.) concretely. A alkyl group , a aryl group , a cycloalkyl group , a aralkyl group , a alkoxy group , a cycloalkadienyl group , a sulfur-containing hydrocarbon residue , it isdesirable as hydrocarbon residue in Formula to be a nitrogen-containing hydrocarbon residue or a phosphorus-containing hydrocarbon residue etc.

アルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、ヘキシル基、オクチル基、２－エチルヘキシル基、デシル基、オレイル基等が例示され、アリール基としては、フェニル基、トリル基等が例示され、シクロアルキル基としては、シクロペンチル基、シクロヘキシル基、シクロオクチル基、ノルボルニル基、ビシクロノニル基等が例示され、アラルキル基としてはベンジル基、ネオフイル基等が例示される。

As alkyl group, methyl group , ethyl group , propyl group , iso propyl group , butyl group ,the hexyl group , octyl group , 2-ethylhexyl group , decyl group and oleyl group etc areillustrated. As aryl group, phenyl group and tolyl group etc are illustrated. As cycloalkyl group, cyclopentyl group , cyclohexyl group , cyclo octyl group , norbornyl group and bicyclo nonyl groupetc are illustrated. benzyl group and neophyl group etc are illustrated as aralkyl group.

シクロアルカジエニル基としては、例えば、シクロペンタジエニル基、メチルシクロペンタジエニル基、エチルシクロペンタジエニル基、ジメチルシクロペンタジエニル基、インデニル基、テトラヒドロインデニル基等を例示することができ、アルコキシ基としては、メトキシ基、エトキシ基、プロポキシ基、ブトキシ基等が例示される。含硫黄炭化水素残基としては、チオエチル基、チオフェニル基等が例示され、また、含窒素炭化水素残基としては、ジメチルアミド基、ジエチルアミド基、ジプロピルアミド基等が例示される。

As cycloalkadienyl group, it to be possible to illustrate for exam ple , cyclopentadienyl group ,the methyl cyclopentadienyl group , ethyl cyclopentadienyl group , dimethyl cyclopentadienyl group , indenyl group and tetrahydroindenyl group etc. As alkoxy group, methoxy group , ethoxy group , propoxy group and butoxy group etc areillustrated. As sulfur-containing hydrocarbon residue, thio ethyl group and thio phenyl group etc are illustrated. In addition, dimethyl amide group , diethyl amide group and dipropyl amide group etc are illustrated asthe nitrogen-containing hydrocarbon residue.

その他ビニル基、アリル基、プロペニル基、イソプロペニル基、１－ブテニル基等の不飽和脂肪残基やシクロヘキセニル基等不飽和脂環式基についても例示することができる。ハロゲン原子としてはフッ素、塩素、臭素等を例示することができる。

In addition concerning unsaturated alicyclic group such as unsatur ated aliphatic residue and cyclohexenyl group of vinyl group , the allyl group , propenyl group , isopropenyl group and 1- butenyl group etc it can illustrate. fluorine , chlorine and bromine etc can be illustrated as the halogen atom.

これらのジルコニウム化合物またはハフニウム化合物を前述の無機酸化物担体に担持させて用いることももちろん可能である。

Bearing doing these zirconium compound or hafnium compound i n aforementioned inorganic oxide carrier, also it ispossible of course to use.

本発明の超高分子量ポリオレフィン粉末の製造方法に用いる有機金属化合物としては、チグラー型触媒の一成分として知られている周期律表Ｉ～IV族の有機金属化合物を使用できるが、一般式

As organometallic compound which is used for production metho d of ultrahigh molecular weight polyolefin powder of this invention, isknown as one component of Ziegler type catalyst organometallic compound of Periodic Table I to Group IVwhich can be used, but General Formula

R_nAlX_{3-n}

（ただしRは炭素数１～20のアルキル基、アリール基またはアルコキシル基、Xはハロゲン原子、nは$0<n\leqq 3$、なお、$N\geqq 2$の場合、各Rは同一でも異なってもよい）で示される有機アルミニウム化合物、および一般式

R_nAlX_{3-n}

Organoaluminum compound which is shown with (However as for R carbon number 1 to 20 alkyl group , aryl group or alkoxy group . As for X halogen atom . As for n $0<n\leq 3$, furthermore, in case of $N\geq 2$, eachR being identical, is possible to differ.). And

R_2Zn

（ただしRは炭素数１～20のアルキル基であり、二者同一でもまた異なっていてもよい）で示される有機亜鉛化合物が好ましく、またこれらの混合物でもよい。

有機アルミニウム化合物としては、例えばトリエチルアルミニウム、トリイソブチルアルミニウム、トリｎ－ヘキシルアルミニウム、ジエチルアルミニウムクロリド、モノエトキシジアルキルアルミニウム、ジエトキシモノアルキルアルミニウム等が挙げられ、また、トリアルキルアルミニウムと水との反応で得られる一般式

$$\left(\begin{array}{c} R \\ | \\ Al - O \end{array} \right)_n$$

で表わされる化合物（ここではRは炭素数１～18の炭化水素基を、ｎは２≦ｎ≦100、好ましくは２≦ｎ≦50を示す）等を用いることもできる。

有機金属化合物の使用量は特に制限はないが通常遷移金属化合物に対して0.1～1000mol倍使用することができる。

重合反応は実質的に酸素、水等を絶った状態で気相状態または前記触媒に対して不活性溶媒、例えばブタン、イソブタン、ペンタン、ヘキサン、オクタン、デカン、ドデカン等の脂肪族系炭化水素、シクロペンタン、シクロヘキサン等の脂環族系炭化水素、ベンゼン、トルエン等の芳香族系炭化水素、石油留分等の存在下、またはモノマー自体を溶媒として行われる。重合温度は生成する超高分子量ポリオレフィンの融点未満、通常－20～110℃、好ましくは０～90℃の範囲であることが望ましい。

重合温度が得られる超高分子量ポリオレフィンの融点以上の場合は、後工程である延伸段階において、20倍以上に延伸することができなくなり好ましくない。

重合圧力は通常０～70kg/cm^{2}G、好ましくは０～60kg/cm^{2}Gの範囲である。

分子量の調節は重合温度、重合圧力、触媒の種類、触媒成分のモル比、重合系中への水素添加等の重合条件を変化させることにより可能であり、特に制限はない。

もちろん、水素濃度、重合温度等の重合条件の異なった

general formula ,

R_2Zn

Organozinc compound which is shown with (However R is carbon number 1 to 20 alkyl group, is identical and it is possible todiffer.) is desirable, in addition is goodeven with these mixture.

As organoaluminum compound, listing for example triethyl alum inum , triisobutyl aluminum , tri n- hexyl aluminum , diethyl aluminum chloride , the mono ethoxy dialkyl aluminum and diethoxy mono alkyl aluminum etc. In addition, general formula which is obtained with reaction with trialkyl aluminumand water,

So it is possible also to use compound (Here as for R hydrocarbon group of carbon number 1 to 18. n shows 2≤n≤ 10 0 and preferably, 2≤n≤50.) etc which is displayed.

As for amount used of organometallic compound there is not esp ecially restriction,but. Usually, 0.1 to 10 00 mol time you can use vis-a-vis transition metal compound.

As for polymerization reaction with state which cuts off oxygen and wateretc in actual, gas state , or vis-a-vis aforementioned catalyst, aliphatic type hydrocarbon of inert solvent , for example butane , isobutane , pentane , hexane , octane , decane and the dodecane etc. cycloaliphatic hydrocarbon of cyclopentane and cyclohexane etc. aromatic type hydrocarbon of benzene and toluene etc, petroleum distillate etc, under existing of these, or it is done monomer itself as solvent, As for polymerization temperature under melting point of ultrahigh molecular weight polyolefin which is formed, it isdesirable usually to be a range of -20 to 1 10 °C and preferably, 0 to 90 °C.

When it is a ultrahigh molecular weight polyolefin melting point or higher where you can obtain polymerization temperature, drawing itbecomes impossible above 20 times in drawing step which is a postprocessing, isnot desirable.

Polymerization pressure is range of 0 to 70 kg/cm^{2}G and prefer ably, 0 to 60 kg/cm^{2}G usually.

As for adjustment of molecular weight, polymerization temperat ure and polymerization pressure . kind of catalyst. mole ratio of catalyst component, hydrogenation to in polymerization system, such as polymerization condition by changing it is possible, there is not especiallyrestriction.

Of course, it can execute polymerization reaction of multiple ste

２段階ないしそれ以上の多段階の重合反応も何ら支障なく実施できる。

ps 2-stage or more wherethe polymerization condition of hydrogen concentration , polymerization temperature etc differs without hindrance.

かくして、粉末状の超高分子量ポリオレフィンが得られる。

You can obtain ultrahigh molecular weight polyolefin of powder.

２）圧延および／または延伸

2) rolling and / or drawing

かくして得られる超高分子量ポリオレフィン粉末を圧延および／または延伸する方法としては、溶融工程を経たのち圧延および／または延伸する方法、多量の溶媒に溶解したのちシート状のゲル状物とし、しかるのち圧延および／または延伸する方法、および溶媒に溶解させることなくまた溶融工程を経ることのない固相状態において圧延および／または延伸する方法等が挙げられ、特に、固相状態において圧延および／または延伸する方法の採用が好ましい。

Likewise as methodwhich rolling and drawing is done ultrahigh m olecular weight polyolefin powder which is obtained, method which rolling and / or drawingis done after passing melt step, amethod which fter melting in solvent of large amount, it makes gelled product of the sheet, rolling and / or drawing is done. or method which without melting in solvent, in solid phase state which in addition doesnot pass melt step, rolling and / or drawingisdone. Such as listing. Especially, adoption of method which rolling and drawing is done is desirablein solid phase state.

固相状態において圧延および／または延伸する方法としては、前記の超高分子量ポリオレフィン粉末を、ポリオレフィンの融点未満の温度において圧延および／または延伸するものであり、通常、圧延および／または延伸に先立ち、ポリオレフィンの融点未満の温度での圧縮成形工程を経る方法を採用することが好ましく、圧縮成形後、圧延し、しかるのち延伸する方法を採用することが最も好ましい。

In solid phase state, as method which rolling and drawing is done, aforementioned ultrahigh molecular weight polyolefin powder, in temperature under melting point of polyolefin,it is something which rolling and drawing is done. Usually, it precedes rolling and drawing, it is desirable to adopt methodwhich passes compression molding step with temperature under melting point of polyolefin. After compression molding, it is most desirable to adopt method which the rolling drawing is done.

圧縮成形の方法は、特に限定されるものではなく、バッチ式、連続式のいずれでもよい。バッチ式圧縮成形方法としては、スライド式、回転式等の各種の機械を用いる方法が挙げられる。連続式圧縮成形方法としては、種々の方法があり、例えば、上下に対向した一対のエンドレスベルトの間に前述の混合物を挟み、エンドレスベルトを移動させつつ圧縮成形する方法等が挙げられる。本発明においては、作業性、長尺材料の生産性から連続式の採用がより好ましい。

Method of compression molding is not something which especiall y is limited,it is good with whichever of batch type , continuous system. As batch type compression molding method, you can list method which uses various machine of the slide type , rotary type etc. As continuous system compression molding method, there is a various methods. for example ,putting between aforementioned mixture between endless belt of thepair which opposes to top and bottom, while moving endless belt, you can listthe method etc which compression molding it does. Regarding this invention, adoption of continuous system is more desirable from theproductivity of workability , elongation material.

かかる連続式の圧縮成形工程についてさらに詳細に説明する。まず、用いる装置の一つの具体例である第１図に基づき簡略に説明する。

Furthermore you explain in detail concerning compression moldi ng step of this continuous system. First, you explain simply on basis of Drawing 1 which is a concrete exampleof one of equipment which is used.

この装置は、基本的にはロール１～４により張力がかけられた上下に対向させた一対のエンドレスベルト5,6と、このエンドレスベルトを介し、粉末材料を加圧するための加圧プレート７と、加圧プレートとエンドレスベルトとの間に回転自在で互いに連結されたローラー群８とからなる加圧手段を有している。

As for this equipment, in basic, has possessed pressurized means which consists of endless belt 5,6 of pair which opposesto top and bottom where tension was applied by roll 1 to 4 , pressurized plate 7 in order pressurized to do powder material through this endless belt, roller group 8 which with pressurized plate and endless belt is connected mutuallywith freely rotating.

本発明における加圧手段は、エンドレスベルトの内側に設けられた加圧プレートおよび加圧プレートとエンドレスベルトとの間に回転自在な互いに連結されたローラー群からなる。加圧プレートとエンドレスベルトとの間に介在さ

As for pressurized means in this invention, consists of pressuriz ed plate which is provided in theinside of endless belt. and freely rotatable roller group which isconnected mutually with pressurized plate and endless belt . As roller groupwhich freely rotatable which

せる回転自在な互いに連結されたローラー群としては、そのローラー群におけるローラーの回転軸がエンドレスベルトの進行方向にほぼ垂直に配置され、かつ相互に接触しない程度に密接させて多数配列させたものが適当である。

lies between with pressurized plate and endless belt is connected mutually, rotational axis of roller in roller group in advancing direction of endless belt isalmost arranged in vertical. At same time denseness touching in extent which does notcontact mutually, large number those which are arranged are suitable.

これらのローラーは、両端の中心軸がそれぞれチェーン９で固定され、加圧プレートの前後に配設したスプロケット10にこのチェーンを噛み合わせることにより、ローラー群をエンドレスベルトの走行速度の1/2程度の速度で走行させるのがよい。

As for these roller, center axis of both ends is locked respectivel y withthe chain 9. roller group it makes run with rate of 1/2 extent of running speed of theendless belt is good to sprocket 10 which is arranged in before and after of the pressurized plate, by engaging this chain.

このローラー群はエンドレスベルトと加圧プレートとの間にフレーム等に固定して介在させてもよい。

This roller group may lie between with endless belt and pressurize d plate, locking inthe frame etc.

加圧プレートとしては、ローラー群に接する面が平滑であり、かつ圧力に均一に伝達できるものである限り特に制限されない。

As added pressure plate, if surface which touches to roller group i s smooth,is something which at same time can be transmitted to uniform inthe pressure, especially it is not restricted.

加圧プレートのエンドレスベルト走行方向の長さは、特に制限されないが通常30～400cm、好ましくは50～200cm程度が適当である。

Length of endless belt running direction of pressurized plate is no t restricted especially, butusually 30 to 400 cm and preferably, 50 to 200 cm extent are suitable.

加圧プレートは、エンドレスベルトを介して超高分子量ポリオレフィン粉末を加圧することが、第１義的な役割であるが、同時に被圧縮物の加熱手段としても使用することも可能である。また、第２図に示すように、加圧プレート内に加熱手段11を配設し、加圧プレートからローラー群、エンドレスベルトを経て被圧縮物を加熱したり、第１図に示すようにエンドレスベルトに近接させて予備加熱器12を配設して加熱するのが実際的に便宜である。

As for pressurized plate, through endless belt, what ultrahigh mol ecular weight polyolefin powder pressurized is done,is first role. In same time as heating means of matter being compressed also it is possible to use. In addition, as shown in Drawing 2, heating means 11 is arranged inside the pressurized plate. Passing by roller group and endless belt from pressurized plate, it heats matter being compressed. As shown in Drawing 1, bringing close to endless belt, arranging the preheater 12, it is convenient actually to heat.

加圧プレートへの加熱手段11の配設態様としては、断熱部13を設けた上で加圧プレート内に電熱ヒーターを埋め込んでもよいし、加圧プレート内に熱媒体の循環流路を配設して熱媒体を用いて加熱してもよい。

As alignment embodiment of heating means 11 to pressurized pla te, after providing insulating part 13, itis possible to imbed electric heater inside pressurized plate. Arranging circulating fluid line of hot medium inside pressurized plate, it is possible toheat making use of hot medium.

この例示された装置を用いて本発明の製造方法を実施するには、まず、ホッパー14内に投入された超高分子量ポリオレフィン粉末を下方のエンドレスベルト６上に落下させる。

Production method of this invention is executed this making use of equipment whichwas illustrated, first, ultrahigh molecular weight polyolefin powder which is thrown inside hopper 14, itfalls on endless belt 6 of beneath.

エンドレスベルトの走行速度は、加圧プレートの長さ、圧縮条件にも依存するが、通常は10～500cm/min、好ましくは50～200cm/min程度が適当である。エンドレスベルト上に乗った超高分子量ポリオレフィン粉末は、ドクターブレードにより所定の断面形状となし、必要により加熱器により予備加熱された後、上下のエンドレスベルトによる挟圧部まで移動され、次いでローラー群と加圧プレートとが配設された圧縮部へ移行される。ここで、油圧シリンダー（図示せず）からの圧力が油圧ピストン15、加圧プレート７へと伝達され、さらにローラー群、エンドレスベルトを経て被圧縮物に圧縮力が加えられる。この時、加熱体からの熱も同様にローラー群、エンドレスベルトを経て被圧縮物に

Running speed of endless belt, depends on length of pressurized p late, also the compression condition, but usually 10 to 500 cm/min and preferably, 50 to 200 cm/min extent are suitable. predetermined cross section shape it forms ultrahigh molecular weight polyolefin powder which rode on endless belt, with doctor blade . After being done with heater in accordance with necessary thepreheating, it is moved to squeezed part due to endless belt of top and bottom. It moves to compression part where roller group , pressurized plate is arranged next. Here, pressure from hydraulic cylinder (not shown) is transmitted to with hydraulic piston 15, pressurized plate 7. Furthermore passing by roller group , endless belt, it can add to matter being compressed compressive force.

伝達され、被圧縮物の温度が所定の温度に保持される。

This time, also heat from heater passing by roller group , endless belt in sameway, it is transmitted by matter being compressed. temperature of matter being compressed is kept in predetermined temperature.

このようにして圧縮成形されたシートは、ロール部を通過した後、エンドレスベルトから離れる。このようにして圧縮成形シートが連続的に成形される。

Sheet which compression molding is done, roll part after passing, leavesfrom endless belt this way. compression molded sheet forms in continuous this way.

本発明における圧縮成形時の圧力は広い範囲内において選定され得るが、通常、0.01MPa～2GPa、好ましくは1～500MPaの範囲内において選定されることが望ましい。特に連続式の場合には、方法を適宜選択することにより、通常0.01～10MPa、好ましくは0.1～5MPa程度の低圧力で充分な圧縮成形が可能となる場合がある。また、圧縮成形時の温度は超高分子量ポリエチレンの融点未満の温度であることが好ましく、通常20℃～融点未満、好ましくは90～140℃、さらに好ましくは110～135℃の範囲である。

Pressure at time of compression molding in this invention can be selected ininside wide range. It is desirable usually, to be selected in inside range of the0.01 MPa to 2 GPa and preferably, 1 to 500 MPa. Especially in case of continuous system, usually with low pressure of 0.01 to 10 MPa and preferably, 0.1 to 5 MPa extent, there are times when satisfactory compression molding becomes possible byselecting method appropriately. In addition, as for temperature at time of compression molding, it isdesirable to be a temperature under melting point of ultrahigh molecular weight polyethylene. Usually under 20 °C to melting point, preferably, 90 to 140 °C , furthermore it is a range of thepreferably, 1 10 to 135 °C.

次に、圧延工程について説明する。圧延方法としては、ロール圧延等の公知の方法を用いることができ、超高分子量ポリオレフィンあるいは前記超高分子量ポリオレフィン圧縮成形シートを溶融させることなく固相状態に保持したまま回転方向の異なる圧延ロールにより挟圧して圧延シートまたはフィルムが得られる。この時、圧延操作により材料の変形比は広く選択することができ、通常、圧延効率（圧延後の長さ／圧延前の長さ）で1.2～20、好ましくは1.5～10の範囲とするのが望ましい。この時の温度としては、通常20℃以上本発明で用いる超高分子量ポリエチレン粉末の融点未満、好もしくは50℃以上該融点未満、さらに好ましくは90～140℃、特に好ましくは110～135℃の範囲の温度で圧延操作を実施することが望ましい。もちろん、上記圧延操作を一回以上多段圧延することもできる。

Next, you explain concerning rolling step. As rolling method, it to be possible to use known method of rolling etc. ultrahigh molecular weight polyolefin or aforementioned ultrahigh molecular weight polyolefin compression molded sheet melt it does not do, is kept inthe solid phase state, rolling sheet or film is obtained with rolling roll where rotation directiondiffers putting between. As for deformation ratio of material, it to be possible to select widely, this time, with rolling operation . It is desirable usually, to make range of 1.2 to 20 and preferably, 1.5 to 10with rolling efficiency (length after rolling. / length before rolling). As temperature of this time, under melting point of ultrahigh molecular weight polyethylene powder which usuallyis used with 20 °C or higher this invention. Under friendship or 50 °C or higher said melting point, furthermore with temperature of rangeof preferably, 90 to 140 °C and particularly preferably, 1 10 to 135 °C, it is desirable to execute rolling operation. Of course, one time or greater multistage rolling above-mentioned rolling operation also it is possible todo.

延伸方法としては、種々の方法があり、その方法としては本発明の目的を損なわない限り特定されないが、例えばまず、加熱手段としては熱風延伸、シリンダー延伸、ロール延伸、熱板延伸等がある。また延伸張力をかける手段としてニップロール間で延伸したりクローバーロール、多段ロール間で張力をかけたり、ネルソンロール方式で延伸張力を保持しながら延伸することも可能である。

As drawing method, if there is a various methods, it does not imp air objective of thethis invention as method, it is not specific . There is a hot air drawing , a cylinder drawing , a roll drawing and a hot plate drawing etc for example first, asthe heating means. Also it is possible in addition while drawing doing between thenip roll as means which applies drawing tension and/or applying tensionbetween clover roll and multistage roll, keeping drawing tension with Nelson roll type thedrawing to do.

温度は、被延伸物の融点未満の範囲内、通常20～160℃、好ましくは60～150℃、さらに好ましくは90～145℃で行われる。また、延伸工程も一段だけでなく多段で行うこともできる。この場合、一段目より二段目のほうを高い温度で行うのが好ましい。

Temperature, inside range under melting point of matter being dr awn, usually the20 to 160 °C and preferably, 60 to 150 °C , furthermore is done with preferably, 90 to 145 °C. In addition, doing with multistage stretching process or not only a one step it ispossible. In this case, it is desirable to do with temperature which second stage ishigher than first stage.

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延伸速度は、引張延伸の方法、ポリマー分子量、組成比により異なるので、適宜に選択可能であり、通常1mm/min～500m/minの範囲である。特に回分式延伸の場合は、通常、1～500mm/min好ましくは1～100mm/min、さらに好ましくは5～50mm/minの範囲である。また、連続延伸の場合は、通常0.1～500m/min、好ましくは1～200m/min、さらに好ましくは10～200m/minの範囲内である。一般に経済性を考慮すれば、高速度の設定がより好ましい。

Because drawing rate differs method of tensile drawing, dependin g upon the polymer molecular weight and composition ratio , it is a selectable appropriately, is a range of the1 mm/min to 500 m/min usually. Especially in case of batch system drawing, usually 1 to 500 mm/min preferably, 1 to 10 0 mm/min , furthermore it isa range of preferably, 5 to 50 mm/min. In addition, in case of continuous drawing, usually 0.1 to 500 m/min and preferably, 1 to 200 m/min ,furthermore it is inside range of preferably, 10 to 200 m/min. If economy is considered generally, setting of high speed is moredesirable.

延伸倍率は、高倍率にするほど高強度製品が得られるため、できるだけ延伸倍率を高めることが望ましく、通常1.5～50倍、好ましくは2～40倍、さらに好ましくは2～30倍である。また圧延と延伸とを組合わせる場合には、圧延および延伸のトータル延伸倍率が、通常20倍以上、好ましくは60倍以上、さらに好ましくは80～200倍とすることが望ましい。

As for draw ratio, because you can obtain extent high strength pr oduct which ismade high multiples, as much as possible it is desirable to raise thedraw ratio. Usually 1.5 to 50 time and preferably, 2 to 40 time, furthermore it is preferably, 2 to 30 time. In addition when it combines with rolling and drawing, total draw ratioof rolling and drawing, usually above 20 times. preferably, 60 times or more , furthermore it is desirable to make preferably, 80 to 200 time.

このような固相状態における延伸法を適用し、超高分子量ポリエチレンを原料として用いた場合では、引っ張り強度が、通常0.7GPa以上、一般的には1.5GPa以上、さらに一般的には2GPa以上であり、また引っ張り弾性率は、60GPa以上、一般的には80GPa以上、より一般的には120～150Gpaの範囲であるポリエチレン延伸材料（未フィブリル化）が得られる。

Drawing method in this kind of solid phase state is applied. With when it uses ultrahigh molecular weight polyethylene as raw material, tensile strength, above 1.5 GPa,furthermore is above 2 GPa usually above 0.7 GPa, generallygenerally. In addition as for tensile elastic modulus, above 60 GPa, you can obtain thepolyethylene drawing material (unfibrillated) which above 80 GPa, from is a range of 120 to 150Gpa generallygenerally.

なお、前述した通り、超高分子量ポリオレフィン粉末を溶剤にとかしてシート状のゲル状物としたものをロール圧延し、しかるのち引張延伸するか、またはこのゲル状物を引張延伸することによっても延伸ポリオレフィンを製造することができる。この場合のロール圧延および引張延伸の条件は上記の条件と同様であることが好ましい。

Furthermore, as mentioned earlier, melting ultrahigh molecular w eight polyolefin powder in solvent, therolling it does those which it makes gelled product of sheet. After that tensile drawing it does, or by tensile drawing doing this gelled product, drawing polyolefin can be produced. As for condition of rolling in this case and tensile drawing, it isdesirable to be similar to above-mentioned condition.

３）超音波処理の方法

3) method of ultrasonic treatment

この発明のフィブリル化ポリオレフィン材料は、前記の延伸ポリオレフィンを、超音波処理することにより得られるものであり、以下にその超音波処理の条件を示す。

As for fibrillated polyolefin material of this invention, it is some thing which is obtained bythe ultrasonic treatment doing aforementioned drawing polyolefin, condition of ultrasonic treatment ofthe below is shown.

超音波を伝達する媒体は、超高分子量ポリオレフィンに対して膨潤、溶解作用を有しないものであれば特に制限されないが、例えば、水やメタノール、エタノール、iso－プロピルアルコール等のアルコール類、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類等が挙げられ、経済性の面から通常、水が好ましく用いられる。使用する超音波の発振周波数は、通常20～500kHz、好ましくは20～300kHz.さらに好ましくは20～200kHzである。出力は使用する延伸物の形態や処理量によって異なるが、通常、媒体液100mlに対して1W～100kW、好ましくは10W～75kW、さらに好ましくは10W～50kWが好ましい。処理温度は、通常、5～90℃、好ましくは10～70℃、さ

As for medium which transmits ultrasound, if it is something whic hit does not possess swelling , dissolving action, especially is not restricted vis-a-visthe ultrahigh molecular weight polyolefin. alcohols of for example , water and methanol , ethanol and iso-propyl alcohol etc. Listing polyvalent alcohols etc of polyethylene glycol , polypropylene glycol and glycerine etc. It can use water usually, desirably from aspect of economy. oscillation frequency of ultrasound which you use, usually 20 to 500 KHz and preferably, 20 to 300 KHz ,furthermore is preferably, 20 to 200 KHz. Output differs depending upon morphology and treated amount of drawn articlewhich is used, but 1W to 10 0 kW and preferably, 10 W to 75 kW , furthermore

らに好ましくは20～65℃の範囲であり、処理時間は、通常、１分～５時間、好ましくは５分～２時間、さらに好ましくは10分～１時間の範囲である。

preferably, 10 W to 50 kW isdesirable usually, vis-a-vis medium liquid 10 0 ml. treatment temperature, usually, 5 to 90 °C and preferably, 10 to 70 °C , furthermore is rangeof preferably, 20 to 65 °C. treatment time, usually, 1 min to 5 hours and preferably, 5 min to 2 hours , furthermore is rangeof preferably, 10 min to 1 hour.

超音波処理の方法は、特に限定されるものではないが、例えば、超音波伝達媒体で満たされた槽の中に複数のロールを浸漬し、これらのロールに試料を沿わせて、この槽の中で所定の時間試料が滞留できるようなロール速度を選んで、超音波処理する方法が挙げられる。

Method of ultrasonic treatment is not something which especiall y is limited. for example , roll of multiple immersion is done in tank which is filledup with ultrasound transmission medium, making sample these roll parallel, in this tank predetermined time sample,choosing kind of roll rate which residence it is possible, you canlist method which ultrasonic treatment it does.

なお、ポリオレフィンは極性基がなく、表面が不活性なために、表面への印刷、あるいは接着が一般的に困難である。したがって必要に応じて超音波処理する前、あるいは好ましくは超音波処理後に、延伸シートまたはテープをコロナ放電処理、プラズマ処理、薬品酸化処理、紫外線処理、あるいは火焔処理等の表面処理が行われる。

Furthermore, polyolefin is not a polar group, surface because of inert,printing or glueing to surface is difficult generally. Therefore according to need, before ultrasonic treatment or after preferably, ultrasonic treatment. surface treatment of corona discharge treatment , plasma treatment , chemical oxidation treatment , ultraviolet treatment or flame treatmentetc is done drawing sheet or tape.

かくして、フィブリル化ポリオレフィン材料が得られるが、これらは0.1～50μmのフィブリル構造を有しているため、柔軟性を有しかつ著しく増大した表面積を有するため、他樹脂との積層化が容易な材料である。しかも、フィブリル化ポリオレフィン材料は、高強度を有し、通常0.5～3GPa、より一般的には１～2.5GPaの引張強度を有するものである。

You can obtain likewise fibrillated polyolefin material, but these b ecause it has possessed fibril structureof 0.1 to 50 μm, have flexibility. At same time in order to possess surface area which is increasedconsiderably, it is a material where lamination of other resin iseasy. Furthermore, as for fibrillated polyolefin material, high strength possessing. Usually 0.5 to 3 GPa , from generally it is something which possesses thetensile strength of 1 to 2.5 GPa.

〔実　施　例〕

(Working Example)

以下に、具体的に実施例により本発明を詳述するが、この発明はこれらの例示により何ら限定されるものではない。

Below , concretely this invention is detailed with Working Exam ple , but thisinvention what is not something which is limited with these illustrations.

実施例１

Working Example 1

135℃デカリン中における極限粘度が17.6dl/gであり、融点142℃の超高分子量ポリエチレン粉末を下記の仕様（概略第１図）のダブルベルト式連続圧縮成形機を用いて温度135℃、圧力約45kgf/cm^{2}の条件で、厚さ1.1mm,幅100mmのシートを連続成形した。

Limiting viscosity in in 135 °C decalin is 17.6 dl/g. ultrahigh m olecular weight polyethylene powder of melting point 142 °C, making use of double belt type continuous compression molding machine of below-mentionedspecification (outline Drawing 1), with condition of temperature 135 °C and pressure about 45 kgf/cm^2, sheet of thickness 1.1 mm , width 10 0 mm thecontinuous molding was done.

圧縮成形機仕様：

Compression molding machine specification :

1. ロール　　径　500　mm　面長　300mm
2. スチールベルト　厚み　0.8mm　幅　200mm
3. 小口径ローラー　径　12　mm　面長　250mm
4. 加圧プレート　長さ　600　mm　幅　200mm

1. roll diameter 500 mm surface length 300 mm
2. steel belt thickness 0.8 mm width 200 mm
3. small diameter roller diameter 12 mm surface length 2 50 mm
4. pressurized plate length 600 mm width 200 mm

次に、このシートをロール間の間隙65μm、ロール表面温度135℃の一対のロールの間に供給し、圧延を行い７倍の長さに伸長した。

さらに、得られた圧延シートを幅30mmにスリットしてテープ状とし、下記の仕様の延伸装置を使用して引張延伸を行った。引張延伸は表１の条件で３回繰り返し、合計延伸倍率63倍の延伸材料を得た。

延伸装置仕様：

1. 加熱体

予熱用金属ロール３本、径　250mmφ　面長　200mm

延伸用金属ロール１本、径　125mmφ　面長　200mm

ロール内部に熱媒体用オイルを循環

ロール間距離は何れも30mm

2. 冷却用金属ロール３本、径　250mmφ　面長　200mm

ロール内部に水を循環

3. ニップロール

入口側:200φシリコンゴムロールが余熱用金属ロール２本に対してニップ

出口側:200φシリコンゴムロールが冷却用金属ロール２本に対してニップ

表　　　1

	金属ロール温度（℃）		ニップロール周速度（m／分）		延伸倍率
	予熱用	延伸用	入口側	出口側	（倍）
1回目	135	140	1	3	3
2回目	140	145	4	8	2
3回目	140	145	10	15	1.5
合計					9

前述のポリエチレン延伸材料を長さ500mmに切断し、それに重りをつけて水200mlを満たした300mlのビーカー中に浸漬させる。超音波発生器（発振周波数および出力はそれぞれ40kHzおよび55Wである）水100mlを満たし、上記ビーカーを浸して25℃、30分間超音波処理した。

Next, it supplied this sheet, gap 65 μm between roll, between theroll of pair of roll surface temperature 135 °C, did rolling and elongation did inthe length of 7 time.

Furthermore, slitting doing rolling sheet which is acquired inthe width 30 mm, it makes tape. Using drawing equipment of below-mentioned specification, it did tensile drawing . 3 times it repeated tensile drawing with condition of Table 1, acquiredthe drawing material of total draw ratio 6 3 times.

Drawing equipment specification :

1. heater

Preheating metal roll 3 and diameter 250 mm diameter surface length 200 mm

Drawing metal roll 1 and diameter 125 mm diameter surface le ngth 200 mm

In roll interior hot medium oil circulation.

As for interroll spacing 30 mm .

2. cooling metal roll 3 and diameter 250 mm diameter surface l ength 200 mm

In roll interior water circulation

3. nip roll

Inlet side : 200φ silicon rubber roll vis-a-vis metal roll 2 for exce ss heat nip .

Outlet side : 200φ silicon rubber roll vis-a-vis cooling metal roll 2 nip

Aforementioned polyethylene drawing material is cut off in lengt h 500 mm. Attaching weight to that, immersion it does in beaker of the300 ml which fills up water 200 ml. ultrasound generator (oscillation frequency and output are respective 40 KHz and 55W.) water 10 0 ml filling up. Soaking above-mentioned beaker, 25 °C and 3 0-minute ultrasonic treatment it did.

かくして直径が約１～15μｍのフィブリルを同一方向に有するフィブリル化ポリエチレン材料が得られた。このようにして得られたフィブリル化ポリエチレン材料の一部を切断し、それを電子顕微鏡で観察した像を図３に示した。なお観察倍率は200倍である。

Fibrillation polyethylene material where likewise diameter has fib ril of about 1 to 15 μm in same directionacquired. one part of fibrillation polyethylene material which it acquires in this way is cut off. Image which observes that with electron microscope was shown in Drawing 3. Furthermore observation magnification is 200 time.

実施例２

Working Example 2

135℃デカリン中における極限粘度が16.7dl/gであり、融点143℃の超高分子量ポリエチレン粉末を、プレス機により圧力約100kgf/cm^2、温度130℃において圧縮成形し、厚さ1.0mm、長さ100mm角のシートを得た。

Limiting viscosity in in 135 °C decalin is 16.7 dl/g. ultrahigh m olecular weight polyethylene powder of melting point 143 °C, with press compression molding it does in pressure about 10 0 kgf/cm^2 and temperature 130 °C. sheet of thickness 1.0 mm and length 10 0 mm square was acquired.

次に、こシートは、ロール間の間隙50μｍ、ロール表面温度135℃の一対のロールの間に供給され圧延されて７倍の長さに伸長した。

Next, this sheet is supplied, gap 50 μm between roll, between t heroll of pair of roll surface temperature 135 °C, rolling being done, elongation it did in length of 7 time.

この圧延されたシートから幅50mm、長さ100mmの試料片が切り出されて、恒温槽付引張試験機により135℃、引張速度50mm/minの条件下に、さらに原寸の６倍長となる引張延伸を受け、圧延と引張延伸の合計倍率は42倍となって、幅約15mm、厚さ110μｍのポリエチレン延伸材料が得られた。

Test specimen of width 50 mm and length 10 0 mm was cut fro m sheet which thisrolling is done. With constant temperature tank attaching tensile tester under condition of 135 °C and the strain rate 50 mm/min. Furthermore tensile drawing which becomes 6-fold length of original dimension isreceived. As for total multiplier of rolling and and tensile drawing becoming 4 2 times. polyethylene drawing material of width about 15 mm and thickness 1 10 μm acquired.

上記のポリエチレン延伸材料を300mmに切断し、それを発振周波数が100kHz、出力が75Wである超音波発生器を用いることと、超音波処理時間が20分であることを除いて実施例１と同様に超音波処理した。その結果、実施例１と同様なフィブリル化延伸材料が得られた。なお、該材料は直径が約0.5～10μｍのフィブリルを同一方向に有していた。

Above-mentioned polyethylene drawing material.is cut off in 300 mm. That ultrasonic treatment it did in same way as Working Example 1 excluding factthat ultrasonic treatment time is 2 0 min oscillation frequency making use of ultrasound generator wherethe 10 0 KHz and output are 75W. result , fibrillation drawing material which is similar to Working Example 1 acquired. Furthermore, as for said material diameter had had fibril of about 0.5 to 10 μmin same direction.

比較例１

Comparative Example 1

実施例１において超音波処理を実施しないことを除いて、その他のことは実施例１と同様に行った。得られたポリエチレン延伸材料の電子顕微鏡像写真を第４図に示した。観察倍率は200倍である。

It did other things in same way as Working Example 1 excluding thefact that ultrasonic treatment is not executed in Working Example 1. electron micrograph of polyethylene drawing material which is acquired was shown in theDrawing 4. observation magnification is 200 time.

融点の測定法：

Measurement method of melting point :

試料5mgをDSC装置にセットし、昇温速度５℃／分の条件下に測定し、その吸熱ピーク温度が融点とした。

It set sample 5 mg to DSC equipment, measured under condition o f rate of temperature increase 5 °C per minute,the endothermic peak temperature made melting point.

【図面の簡単な説明】第１図および第２図は本発明において好適に用いられる圧縮成形装置の一例を示す図であり、また第３図および第４図は本発明のフィブリル化ポリオレフィン材料および比較例の方法により得られる材料のフィブリル化された繊維の形状を示す走査型電子顕微鏡写真の

[Brief Explanation of the Drawing(s)] As for Drawing 1 and Drawi ng 2 it is a figure which shows one example ofthe compression molding equipment which is used for ideal in this invention. In addition as for Drawing 3 and Drawing 4, It is a one example of scanning electron microscope photograph which is shown

一例である。

fibrillated polyolefin material of this invention, and shape of fibrilated fiber of material which is obtained and by method of Comparative Example.

1～4……ロール、5, 6……エンドレスベルト、

7……加圧プレート、8……ローラー群、

9……チェーン、10……スプロケット、

11……加熱手段、12……予備加熱機、

13……断熱部、14……ホッパー、

15……油圧ピストン。

1 to 4...... roll and 5,6...... endless belt ,

7...... pressurized plate and 8...... roller group ,

9...... chain and 10 ...... sprocket ,

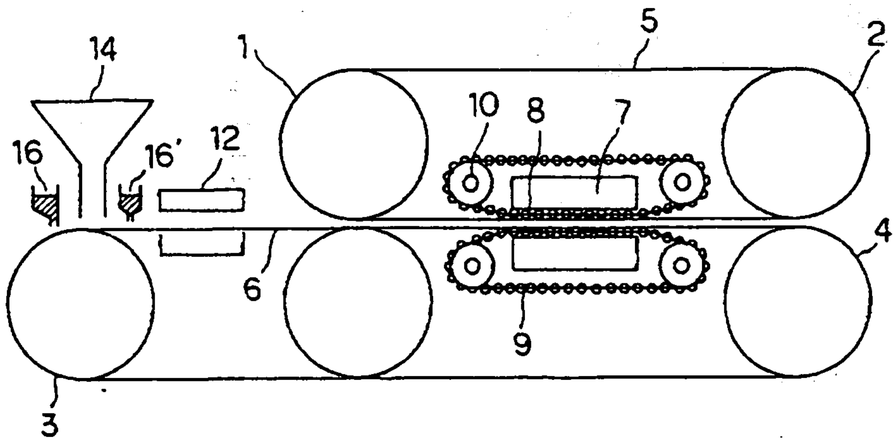
11...... heating means , 12...... preheating machine,

13...... insulating part and 14...... hopper ,

15...... hydraulic piston .

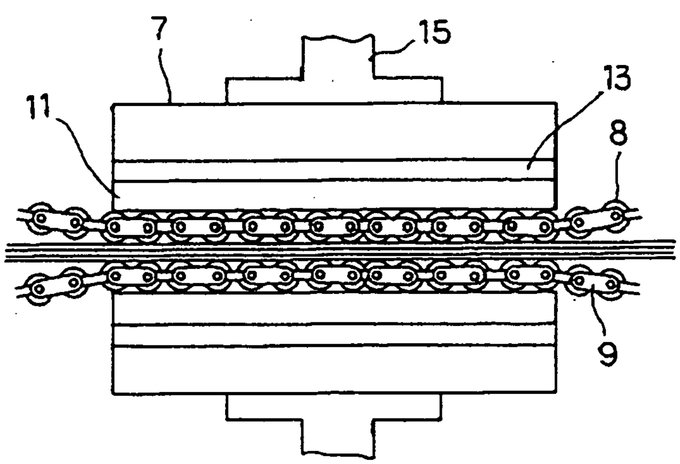
【第１図】

< Drawing 1 >



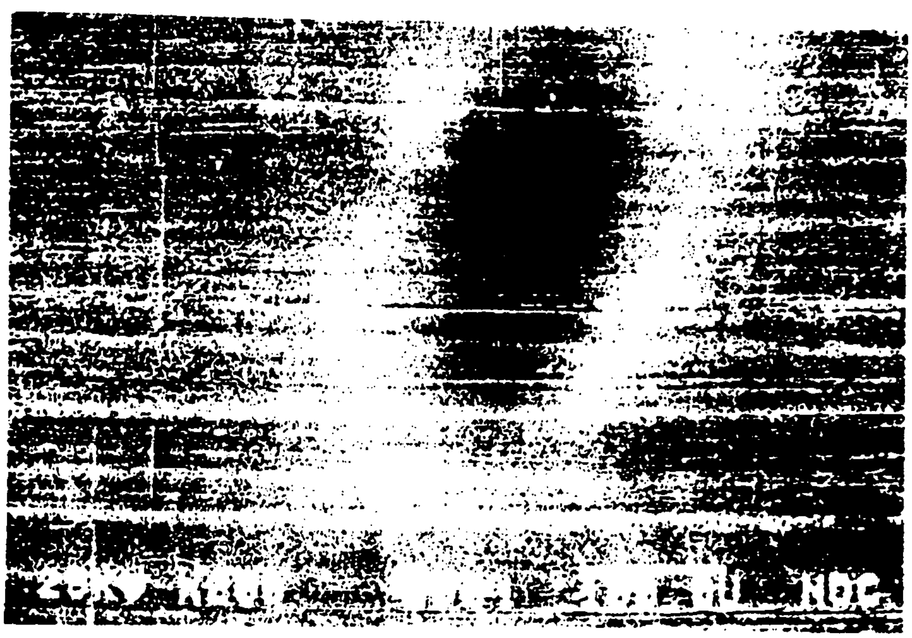
【第２図】

< Drawing 2 >



【第３図】 < Drawing 3 >

【第４図】 < Drawing 4 >



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KOKAI PATENT APPLICATION NO. HEI 4-194068

A POLYOLEFIN MATERIAL WITH A FIBRIL STRUCTURE AND A MANUFACTURING METHOD THEREOF

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Examination Request:	Not requested

A POLYOLEFIN MATERIAL WITH A FIBRIL STRUCTURE AND A MANUFACTURING METHOD THEREOF

[*Fiburiruka poriorefin zairyoh obobi sono seizoh houhoh*]

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[*There are no amendments to this patent.*]

Specification

1. Title of the invention

A polyolefin material with a fibril structure and a production method thereof

2. Claim of the invention

(1) A method of producing a polyolefin material with a fibril structure characterized by the fact that ultrasonic treatment is applied after a rolling compression and/or drawing process.

(2) A polyolefin material with a fibril structure characterized by the fact that the material has a structure composed of fibrils having a diameter of 0.1~50 μm oriented in the same direction.

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3. Detailed description of the invention

[Field of industrial application]

The present invention pertains to a polyolefin material with a fibril structure and a production method thereof, and the invention further pertains to a polyolefin material with a fibril structure having high strength and flexibility for which lamination with other materials can be easily accomplished, and a production method thereof.

[Prior art and Problems to be solved by the invention]

A high strength and high modulus polyolefin material produced by forming an ultra-high molecular weight polyolefin into a sheet or tape and drawing the sheet or tape is known. For example, a method wherein hot-melt mixing is carried out for an ultra-high molecular weight polyethylene and wax, and hot-melt extrusion is carried out for the mixture, and drawing is done after cooling and solidification of the material is described in Japanese Kokai Patent Application No. Sho 59-130313. Also, a method wherein compression molding is performed for a gel-like material produced by cooling an ultra-high molecular weight polyethylene and drawing is performed for the material is described in Japanese Kokai Patent Application No. Sho 60-101032. Furthermore, a method where compression molding is performed for the ultra-high molecular weight polyethylene at a temperature below the melting point and drawing is further performed is described in Japanese Kokai Patent Application No. Sho 63-66207.

Materials such as ultra-high molecular weight polyethylene sheets, tape and fibers made by the above-mentioned methods have high strength and water repellency and are

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light in weight; thus, they are widely used for undersea ropes after forming into a rope, and explosion containment sheets after weaving to produce an open cloth.

However, the above-mentioned ropes and open cloth have high strength, but flexibility is not sufficient due to the high modulus.

Furthermore, when a matrix resin is laminated onto the above-mentioned drawn sheet or tape so as to form a laminate, or a composite material is made with other resins, an adequate adhesive strength cannot be achieved due to limited area of contact with the resin or other material.

[Means to solve the problem]

As a result of much research conducted by the present inventors, they discovered that an effective ultra-high molecular weight polyolefin can be produced when rolling compression and/or drawing is carried out for a specific polyolefin followed by ultrasonic treatment, and that the above-mentioned ultra-high molecular weight polyolefin has high strength and high flexibility as well as high adhesion with other materials, and the present invention was achieved.

In other words, the present invention pertains to a polyolefin material with a fibril structure characterized by the fact that the material has a structure consisting of fibrils with a diameter of 0.1~50 μm oriented in the same direction. And the present invention further pertains to a production method of a polyolefin material with a fibril structure characterized by the fact that an ultrasonic treatment is performed after performing rolling compression and/or drawing.

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In the following, the present invention is further explained in detail.

In the polyolefin material with a fibril structure of the present invention, fibrils having a diameter in the range of 0.1~50, preferably 0.5-30 μm, and especially 1-20 μm, are oriented in the same direction. In general, the orientation direction is the same as the direction of the rolling compression and/or drawing at the time of production of the polyolefin material.

The polyolefin material with a fibril structure of the present invention can be easily produced by rolling compression and/or drawing of an ultra-high molecular weight polyolefin and further providing an ultrasonic treatment. The production process is explained in further detail below.

1) Ultra-high molecular weight polyolefin

For the ultra-high molecular weight polyolefin used in the present invention, a homopolymer of α-olefin with 2~12 carbon atoms, preferably 2~8 carbon atoms, for example, polyethylene, propylene, polybutene-1, etc., a two or more component copolymer consisting of α-olefins having different numbers of carbon atoms, for example, ethylene and an α-olefin with 2~12 carbon atoms, preferably 3~8 carbon atoms (for example, propylene, butene-1, 4- methyl pentene, hexene-1, etc., in general, the amount of the α-olefin is 10 mol% or less, preferably, in the range of 0.01~5 mol%), copolymer of propylene and α-olefin with 4~12 carbon atoms, etc. can be mentioned. Furthermore, copolymers containing dienes, for example, butadiene, 1,4-hexadiene and vinyl norbornane as a comonomer can be mentioned as well.

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In general, the ultra-high molecular weight polyolefin used in the present invention has a molecular weight in the range of 500,000~12,000,000, preferably in the range of 900,000~9,000,000, and in the case of polyethylene or ethylene and α-olefin copolymer, the viscoaverage molecular weight is in the range of 500,000~12,000,000, preferably in the range of 900,000~9,000,000, and especially in the range of 1,200,000~6,000,000, and it is desirable when an ultra-high molecular weight polyolefin having an ultimate viscosity measured in decaline at 135°C in the range of 5~50 dl/g, preferably in the range of 8~40 dl/g and especially, in the range of 10~30 dl/g is used.

When the molecular weight of the polyolefin is 500,000 or below, the mechanical properties of the drawn material or rolled material become inadequate, and on the other hand, when the molecular weight exceeds 12,000,000, the processability becomes poor at the time of compression molding, rolling compression and/or drawing.

Furthermore, the shape of the above-mentioned ultra-high molecular weight polyolefin is not especially limited, and in general, a granular or powder-form material can be used effectively, and those with a particle diameter of 2000 μm or less, preferably, in the range of 1~2000 μm and especially in the range of 10~1000 μm are desirable. Furthermore, flaws are less likely to form when the particle diameter distribution is narrower, and a uniform sheet or film-like material is likely to be produced.

[p. 3]

The ultra-high molecular weight polyolefin having the above-mentioned properties that can be effectively used in the present invention can be produced by performing a polymerization reaction or co polymerization reaction for an α-olefin in the presence of a

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catalytic component containing at least one type of compound containing a transition metal selected among the group IV~VI of the periodic table and an optional organic metal compound.

For the compound containing a transition metal selected among the group IV~VI of the periodic table that structures the catalytic component in this case, in specific terms titanium compound, vanadium compound, chromium compound, zirconium compound, and hafnium compound, etc. can be used effectively. Furthermore, a mixture of the above-mentioned compounds can be used as well.

For the titanium compound, halides, alkoxy halides, alkoxides, halogenated oxides, etc. of titanium can be mentioned, and a tetravalent titanium compound and trivalent titanium compound are especially desirable. In specific terms, those shown in the following general formula

$Ti(OR)_nX_{4-n}$

(wherein, R is an alkyl group with 1~20 carbon atoms, preferably, 1~12 carbon atoms, or an aralkyl group, and X is a halogen atom. Furthermore, n is $0<n<4$.)

can be mentioned for the tetravalent titanium compound, and titanium tetrachloride is especially desirable.

Furthermore, titanium trihalides such as titanium trichloride can be mentioned as trivalent titanium compound, and a trivalent titanium compound produced by performing a reduction reaction for the tetravalent alkoxy titanium halide shown in the following general formula

$Ti(OR)_mX_{4-m}$

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(wherein, R is an alkyl group with 1~20 carbon atoms, or aryl group or alkyl group [sic], and X is a halogen atom. Furthermore, m is $0<m<4$.)
with an organic metal compound selected among the group I~III of the periodic table can be mentioned as well.

Among the above-mentioned titanium compounds, tetravalent titanium compounds are especially suitable.

For the vanadium compounds, halides, alkoxy halides, alkoxides, and halogenated oxides of vanadium can be mentioned, and in specific terms, vanadium tetrahalides such as vanadium tetrachloride, tetravalent vanadium such as tetraethoxy vanadium, pentavalent vanadium compound such as vanadium oxytrichloride, ethoxy dichlorovanadyl, triethoxy vanadyl, and tributhoxy vanadyl, trivalent vanadium compound such as vanadium trichloride, and vanadium triethoxyide, etc. can be mentioned.

Furthermore, a treatment can be carried out for the above-mentioned titanium compound or vanadium compound with one or more types of electron donor compounds. For the electron donor compound, ethers, thioethers, thiol phosphines, stibines, arsines, amines, ketones, esters, etc. can be mentioned.

Furthermore, the above-mentioned titanium compound or vanadium compound can be used in combination with a magnesium compound. For examples of the magnesium compounds used in this case, metal magnesium, magnesium hydroxide, magnesium carbonate, magnesium oxide, magnesium fluoride, magnesium chloride, magnesium bromide, and magnesium iodide, as well as complex salts, complex oxides, carbonates, chlorides or hydroxides containing substances selected from the group consisting of silicon,

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aluminum, calcium, and a magnesium atom; the above-mentioned solid inorganic compounds treated or reacted with an oxygen-containing compound, a sulfur-containing compound, an aromatic hydrocarbon, or a halogen-containing material, furthermore, oxides containing silicon or aluminum mixed with the above-mentioned magnesium compounds, etc. can be mentioned.

When a titanium compound or vanadium compound and a magnesium compound are used in combination, the method used for contact between these materials is not especially limited, and any conventional method can be used.

For the above-mentioned oxygen-containing compound, for example, organic oxygen-containing compounds such as water, alcohols, phenols, ketones, aldehydes, carboxylic acids, esters, polysiloxanes, and acid amides, and inorganic oxygen-containing compounds, for example, metal alkoxides and oxychloride of metals, etc. can be mentioned. For examples of sulfur-containing compounds, inorganic sulfur compounds such as sulfur dioxide, sulfur trioxide, and sulfuric acid can be mentioned. For examples of aromatic hydrocarbons, a variety of unicyclic or polycyclic aromatic hydrocarbon compounds such as benzene, toluene, xylene, anthracene, and phenanthrene can be mentioned. For the halogen-containing substance, compounds such as chlorine, hydrogen chloride, metal chloride, and organic halide can be mentioned.

[p. 4]

For examples of other catalytic systems, a catalytic system wherein a reaction product of an organic magnesium compound such as Grignard compound and a titanium

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compound is used and an organic aluminum compound is used in combination can be mentioned.

As a different example of a catalytic system, a solid catalyst produced by bringing an inorganic oxide such as SiO_2 and Al_2O_3 and the above-mentioned solid catalytic component containing at least magnesium and titanium is used and an organic solubility compound is further used in combination, can be mentioned.

Furthermore, in the above-mentioned catalytic system, the titanium compound can be used as an adduct with the organic carboxylate, and the above-mentioned inorganic solid compound containing magnesium is first brought into contact with an organic carboxylate and used as well. Furthermore, an organic aluminum compound can be used as an adduct with the organic carboxylate without any problem. In addition, a catalytic system prepared in the presence of an organic carboxylate can be used without any problem.

For the chromium compound, a catalyst commonly referred to as a Phillips' catalyst wherein chromium trioxide or a compound composed partially of chromium upon baking is deposited on a carrier made of an inorganic oxide can be mentioned. For an inorganic oxide carrier, silica, alumina, silica-alumina, titania, zirconia, thoria or a mixture thereof can be mentioned and among those listed above, silica and silica-alumina are especially suitable.

For the chromium compound to be deposited, oxides of chromium, compounds composed partially of chromium upon baking, for example, halides, oxyhalides, nitrates, acetates, sulfates and alcolates of chromium can be mentioned, and in specific terms, chromium trichloride, chromylchloride, potassium dichromate, ammonium chromate,

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chromium nitrate, chromium acetate, chromium acetylacetonate, di-tert-butylchromate, etc. can be mentioned.

As a method used for depositing the above-mentioned chromium compound on the carrier, conventional processes such as dip coating, solvent removal, and sublimation can be used, and an appropriate method can be used according to the type of the chromium compound used. The amount of the chromium substance deposited is in the range of 0.1~10 wt% as a wt% of chromium atom for the carrier, in the range of 0.3~5 wt% is especially desirable and in the range of 0.5~3 wt% is especially desirable.

Baking is performed for the carrier with the chromium compound deposited on it and activation is carried out. In general, baking and activation treatments are performed in a non-reducing atmosphere that is essentially free of moisture, for example, in the presence of oxygen, but the treatment can be carried out in the presence of an inert gas under a reducing pressure. It is especially desirable for dry air to be used. Baking is carried out at a temperature of 450°C or higher, preferably at a temperature in the range of 500~900°C for several minutes to several hours, preferably, for 0.5~10 hours. It is desirable when thoroughly dried air is used for baking and the activation is carried out with the material in a fluidized state.

Furthermore, titanates or fluorine-containing salts also can be included at the time of depositing or baking so as to control the degree of activation as usual.

Furthermore, a reduction reaction can be carried out for the catalyst with the above-mentioned chromium compound deposited on it using carbon monoxide, ethylene, organic aluminum compound, etc.

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As examples of zirconium compounds or hafnium compounds, a zirconium compound or hafnium compound wherein a group having a conjugate π-electron as a coordinate can be mentioned, and as a specific example, the compound shown in the general formula below

$R^1{}_aR^2{}_bMR^3{}_cR^4{}_d$

(Wherein, M is a zirconium or hafnium atom, R^1, R^2, R^3 and R^4 are hydrocarbon residue with 1~20 carbon atoms, halogen atom or a hydrogen atom. In this case, at least one among R^1, R^2, R^3 and R^4 is a hydrocarbon residue. And a, b and c satisfy the condition a+b+c+d=4) can be mentioned. For the hydrocarbon residue in the above-mentioned general formula, alkyl group, aryl group, cyclo alkyl group, aralkyl group, alkoxy group, cycloalkadienyl group, sulfur-containing hydrocarbon residue, nitrogen-containing hydrocarbon residue, or phosphor-containing hydrocarbon residue, etc. can be mentioned.

[p. 5]

For the alkyl group, methyl group, ethyl group, propyl group, isopropyl group, butyl group, hexyl group, octyl group, 2-ethyl hexyl group, decyl group, oleyl group, etc. can be mentioned, and for examples of aryl group, phenyl group, tolyl group, etc. can be mentioned. For examples of cyclo alkyl group, cyclopentyl group, cyclohexyl group, cyclooctyl group, norbonyl group, bicyclononyl group, etc. can be mentioned, and for an aralkyl group, benzyl group, etc. can be mentioned.

For cycloalkadienyl group, cyclopentadienyl group, methyl cyclopentadienyl group, ethyl cyclopentadienyl group, dimethyl cyclopentadienyl group, indenyl group, tetrahydro indenyl group, etc. can be mentioned as examples, and for alkoxy group, methoxy group,

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ethoxy group, propoxy group, buthoxy group, etc. can be mentioned. For sulfur-containing hydrocarbon residue, thioethyl group, thiophenyl group, etc. can be mentioned, and for a nitrogen-containing hydrocarbon residue, dimethyl amide group, diethyl amide group, di propyl amide group, etc. can be mentioned.

In addition, unsaturated aliphatic residue such as vinyl group, allyl group, propenyl group, isopropenyl group, and 1-buthenyl group, and unsaturated alicyclic group can be mentioned as well. For examples of halogen atom, fluorine, chlorine, bromine, etc. can be mentioned.

The above-mentioned zirconium compounds or hafnium compounds can be deposited onto the above-mentioned inorganic oxide carriers and used as well.

As for the organic metal compound used for production of the ultra-high molecular weight polyolefin of the present invention, organic metal compounds of groups I~IV of the periodic table also known as a component used in Ziegler catalyst can be used in this case as well, and an organic aluminum compound shown in the general formula below

R_nAlX_{3-n}

(wherein, R is an alkyl group with 1~20 carbon atoms, aryl group, or alkoxyl group, X is a halogen atom, and n is $0<n<3$, and when $n>2$, each R may be the same or different) and an organic zinc compound shown in the general formula below

R_2Zn

(wherein, R is an alkyl group with 1~20 carbon atoms, and they may be the same or different.) are especially desirable, and a mixture of these compounds can be used effectively as well.

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For examples of an organic aluminum compound, triethyl aluminum, triisobutyl aluminum, tri-n-hexyl aluminum, diethyl aluminum chloride, monoethoxy dialkyl aluminum, monoethoxy monoalkyl aluminum, etc. can be mentioned, and a compound produced upon performing a reaction for tolualkyl aluminum and water and is shown in the following general formula

//please insert f

(wherein R is a hydrocarbon group with 1~18 carbon atoms, n is $2<n<100$, preferably, $2<n<50$), etc. can be used as well.

The amount of the organic metal compound used is not especially limited, and in general, the amount of the compound used is in the range of 0.1~1000 times the molar amount of the transition metal compound.

The polymerization reaction is carried out essentially absence of oxygen, water, etc. in a gas-phase or in the presence of an inert solvent for the above-mentioned catalyst, for example, aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, and dodecane, alicyclic hydrocarbon such as cyclopentane and cyclohexane, aromatic hydrocarbon such as benzene and toluene, and petroleum cut, or using the monomer itself as a solvent. The polymerization reaction temperature used is a temperature of below the melting point of the ultra-high molecular weight polyolefin to be produced, in general, a temperature in the range of -20°C~100°C is used, and in the range of 0~90°C is especially desirable.

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When the polymerization reaction temperature used is a temperature of above the ultra-high molecular weight polyolefin to be produced, drawing to more than 20 times cannot be achieved at the time of the drawing process that follows, thus, it is not desirable.

In general, the pressure during the polymerization reaction is in the range of 0~70 kg/cm^2G, and in the range of 0~60 kg/cm^2G is especially desirable.

[p. 6]

An adjustment of the molecular weight can be performed by changing the polymerization reaction condition such as polymerization temperature, polymerization pressure, type of catalyst, molar ratio of the catalytic component, and hydrogen added to the polymerization system, and it is not especially limited.

Needless to say, the above-mentioned polymerization reaction can be divided into two or more stages under different polymerization reaction conditions such as different concentrations of hydrogen and/or polymerization reaction temperature without any problems.

In this manner, a powder-form ultra-high molecular weight polyolefin can be produced.

2) rolling compression and/or drawing

As for the method used for rolling compression and/or drawing for the ultra-high molecular weight polyolefin powder produced as described above, a method where rolling compression and/or drawing are performed after hot-melt process, a method wherein dissolving is performed for the above-mentioned powder in a large amount of solvent to form a sheet-like gel and further performing rolling compression and/or drawing, a method

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wherein rolling compression and/or drawing is performed in a solid state without first dissolving in a solvent or performing a hot-melt process, etc. can be mentioned, and in this case, it is especially desirable when a method where rolling compression and/or drawing is performed under a solid state is used.

As a method used for carrying out the rolling compression and/or drawing under a solid state, a method wherein rolling compression and/or drawing are performed for the above-mentioned ultra-high molecular weight polyolefin powder at a temperature of below the melting point of the polyolefin is desirable, and it is further desirable when a compression molding is performed before the rolling compression and/or drawing at a temperature of below the melting point of polyolefin, and drawing is subsequently performed.

The method used for the compression molding is not especially limited, and either; the batch system or continuous system can be used. For the batch system compression molding method, a method wherein a variety of machines such as a slide system or rotational system are used can be mentioned. For the continuous compression molding method, a method wherein the above-mentioned mixture is placed between a pair of endless belts and compression molding is carried out as the endless belts move. In the present invention, use of a continuous process is especially desirable from the standpoint of working performance and productivity of the long material.

The above-mentioned continuous system compression molding process is explained further in detail below. First, specific example of the device used in the present invention shown in Fig. 1 is used for brief explaination.

The device shown in the fig. has a pair of endless belt 5 and 6 that face each other and imparted with tension by rolls 1~4, pressure plate 7 that applies pressure to the powder material through the above-mentioned endless belts, and a pressure means consisting of group of rollers 8 placed between the pressure plate and endless belt that are free-to-rotate.

The means of applying pressure in the present invention consists of a pressure plate installed inside an endless belt and a group of rollers installed between the pressure plate and the endless belt. For the above-mentioned group of rollers installed between the pressure plate and endless belt, group of rollers is arranged in such a manner that the rotational axis of each roller is nearly perpendicular to the direction of travel of the endless belt and close to one another without actually touching one another.

In the above-mentioned rollers, the axis of rotation at each end is fastened to chain 9, and the group of rollers is moved at approximately 1/2 the transport rate of the endless belt by the engagement of the above-mentioned chain with sprocket 10 installed at the front and back of the pressure plate.

The above-mentioned rollers can be fastened to the frame, etc. and placed between the endless belt and pressure plate.

The type of pressure plate used is not especially limited as long as the surface of the plate that comes in contact with the group of rollers is smooth and the pressure can be uniformly applied.

The length of the pressure plate in the travel direction of the endless belt is not especially limited, and in general, a length in the range of 30~400 cm is suitable and in the range of 50~200 cm is especially desirable.

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The primary function of the pressure plate is application of pressure to the ultra-high molecular weight polyolefin powder through the endless belt, but the pressure plate can also be used as a means for heating the material to be compressed at the same time.

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Furthermore, as shown in Fig. 2, heating unit 11 is arranged inside the pressure plate and heating of the group of rollers, and the material to be compressed can be achieved, or as shown in Fig. 1, pre-heating unit 12 is arranged close to the endless belt and heating can be carried out as well.

As for the arrangement of the heating unit of the pressure plate, a means of insulation 13 is installed and an electric heater can be implanted to the pressure plate, or a circulation path for the heating medium is arranged inside the pressure plate and heating can be carried out through the heating medium as well.

In order to use the production method of the present invention with the above-mentioned device shown in as an example, first, the ultra-high molecular weight polyolefin powder poured into hopper 14 is dropped onto endless belt 6 located below it.

The transport speed of the endless belt depends on the length of the pressure plate and condition used for the compression molding, but in general, the transport speed in the range of 10~500 cm/min is suitable and in the range of 50~200 cm/min is especially desirable. The ultra-high molecular weight polyolefin powder on the endless belt is formed into a shape having a specific cross-section, and pre-heated by the heater, as needed, and transported toward the compression member where the group of rollers and pressure plate are being arranged. At this time, the pressure from the hydraulic cylinder (not shown in the

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figure) is applied to the hydraulic piston 15 and pressure plate 7, and then to the group of rollers and endless belt and the compressive force is ultimately applied to the material to be compressed. In this case, the heat from the heating unit is transmitted to the material to be compressed through the group of rollers and endless belt and the temperature of the material to be compressed is increased at the same time and the temperature of the material to be compressed is maintained at a specific temperature.

The compression molded sheet obtained as described above is then passed through the rolls and is removed from the endless belt. In this manner, continuous molding of a compression-molded sheet is made possible.

The pressure used at the time of compression molding in the present invention can be selected from a wide range, and in general, a pressure in the range of 0.01 MPa~2 GPa is suitable and in the range of 1~500 MPa is especially desirable. In the case of continuous system, an adequate compression molding is made possible under a low pressure in the range of 0.01~10 MPa, preferably in the range of 0.1~5 MPa, through appropriate selection of the method used. Furthermore, it is desirable when the temperature at the time of the compression molding to be a temperature of below the melting point of the ultra-high molecular weight polyethylene, and in general, a temperature in the range of 20°C~below the melting point, preferably, a temperature in the range of 90~140°C, and especially, in the range of 110~135°C, is desirable.

In the following, rolling compression process is explained in detail. For the rolling compression method, a conventional method such as roll molding can be used in this case as well. A solid-form ultra-high molecular weight polyolefin or the above-mentioned

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compression molding sheet of ultra-high molecular weight polyolefin can be pressed by a compression rolls that rotate different directions without melting and a compression molding sheet or film can be produced. In this case, the degree of deformation of the material can be widely selected based on the rolling compression condition used and in general, in the range of 1.2~20, preferably, in the range of 1.5~10, in terms of the rolling compression effect (length before rolling compression/length after rolling compression). As for the temperature used for the rolling compression treatment in this case, a temperature of below the melting point of the ultra-high molecular weight polyethylene used in the present invention is desirable, and a temperature in the range of 50°C to the above-mentioned melting point, and especially, in the range of 90~140°C, and ideally in the range of 110~135°C. Needless to say, a multistage rolling compression process can be used as well.

As for the above-mentioned drawing method, a varieties of methods can be mentioned and the method used in this case is not especially limited, and for example, heating method such as hot-air drawing method, cylinder drawing method, roll drawing method, and hot-plate drawing method, etc. can be mentioned. Furthermore, drawing method with tension such as drawing with nip rolls, clover rolls, and multistage rolls, or drawing under drawing tension by means of the Nelson roll system can be use as well.

The temperature used in this case is below the melting point of the material to be drawn, and a temperature in the range of 20~160°C is suitable, in the range of 60~150°C is especially desirable and in the range of 90~145°C is especially desirable. Furthermore, a multistage drawing can be used for the drawing process, as well. In this case, it is

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desirable when a higher temperature is used for the second stage than the temperature used for the first stage.

The drawing speed varies depending on the drawing method, polymer molecular weight, and composition ratio, and can be selected accordingly, and in general, a drawing speed in the range of 1 mm/min~500 m/min is suitable. Especially when a batch system drawing method is used, in general, the drawing speed used is in the range of 1~500 mm/min, preferably, 1~100 mm/min, and especially, 5~50 mm/min. Furthermore, in the case of the continuous drawing method, the drawing speed used is in the range of 0.1~500 m/min, preferably, 1~200 m/min, and especially, 10~200 m/min. In general, high-speed setting is desirable from the standpoint of cost.

The higher the drawing ratio, the higher the strength of the product produced, thus, it is desirable to increase the drawing ratio as much as possible, and in general, the drawing ratio used is in the range of 1.5~50 times, preferably in the range of 2~40 times, and especially, in the range of 2~30 times. Furthermore, in the case when the rolling compression and drawing are used in combination, it is desirable for the total drawing ratio for the rolling compression and rolling compression and/or drawing to be at least 20 times, preferably, at least 60 times and especially in the range of 80~200 times.

When the drawing method in the above-mentioned solid-phase is used and an ultra-high molecular weight polyethylene is used as a raw material, in general a drawn polyethylene material (before forming fibrils) having a tensile strength of at least 0.7 GPa, preferably at least 1.5 GPa, and especially, at least 2 GPa, and the tensile modulus of at

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least 60 GPa, preferably at least 80 GPa, and especially in the range of 120~150 GPa, can be produced.

Furthermore, as explained above, it is possible to produce a drawn polyolefin when an ultra-high molecular weight polyolefin powder is dissolved in a solvent to form a sheet-like gel and rolling compression is carried out; then, drawing is further performed or drawing is performed for the above-mentioned gel-like sheet. It is desirable for the condition used for the above-mentioned roll rolling compression process and drawing process to be the same as in the condition described above.

3) Method used for the ultrasonic treatment

The polyolefin material with a fibril structure of the present invention is produced by ultrasonic treatment of the above-mentioned drawn polyolefin, and the condition used for the ultrasonic treatment is described below.

The medium used for conduction of the ultrasonic waves is not especially limited as long as the medium is not capable of expanding or dissolving the ultra-high molecular weight polyolefin, and for example, water, alcohols such as methanol, ethernol, and iso-propyl alcohol, polyhydric alcohols such as polyethylene glycol, polypropylene glycol and glycerol can be mentioned, and from the standpoint of cost, water is commonly used. In general, the oscillation frequency of the ultrasonic waves used is in the range of 20~500 kHz, preferably, in the range of 20~300 kHz, and especially, in the range of 20~200 kHz. The output used varies depending on the shape of the material used and the amount of the material used, and in general, an output in the range of 1 W~100 kW is suitable, in the range of 10 W~75 kW is especially desirable and in the range of 10 W~50 kW is especially

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desirable. In general, the processing temperature used is in the range of 5~90°C, preferably in the range of 10~70°C, and especially in the range of 20~65°C, and the processing time used is in the range of 1 min~5 hrs, preferably in the range of 5 min~2 hrs, and especially, in the range of 10 min~1 hrs.

The method used for the above-mentioned ultrasonic treatment is not especially limited, and for example, a method wherein rolls are dipped in a tank filled with an ultrasonic wave transmitting medium, the sample is placed through the above-mentioned rolls and the roll speed capable of retaining the sample for a predetermined time inside the above-mentioned tank is appropriately selected and the ultrasonic treatment is performed can be mentioned.

In general, printability or adhesion at the surface of the polyolefin is made impossible since a polar group is absent and the surface is inert. In this case, a surface treatment is performed for the drawn sheet or tape using a surface treatment method such as corona discharge treatment, plasma treatment, chemical oxidation treatment, ultraviolet treatment and flaming treatment is performed before the ultrasonic treatment, preferably after the ultrasonic treatment.

In this manner, the target polyolefin material with a fibril structure can be produced, and the material has a fibril structure of 0.1~50 μm; thus, an increase in flexibility and the surface area can be achieved, and lamination with a different resins can be made easy. Furthermore, the polyolefin material with a fibril structure produced has a high strength and in general the tensile strength in the range of 0.5~3 GPa, preferably, in the range of 1~2.5 GPa, can be achieved.

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[Application Examples]

In the following, the present invention is further explained in specific terms with application examples, but the present invention is not limited to these examples.

Application Example 1

A sheet having a thickness of 1.1 mm and the width of 100 mm was continuous produced from an ultra-high molecular weight polyethylene having an ultimate viscosity in a 135°C decaline of 17.6 dl/g and the melting point of 142°C using a double-belt type continuous compression molding machine having the specification shown below under a temperature of 135°C and pressure of approximately 45 kgf/cm^2.

Specification of compression molding machine:

1. Roll diameter	500 mm	length 300 mm
2. Steel belt thickness	0.8 mm	width 200 mm
3. Small aperture roller diameter	12 mm	length 250 mm
4. Pressure plate length	600 mm	width 200 mm

Subsequently, the above-mentioned sheet was supplied to the region between a pair of rollers having a separation distance of 65 μm and a roll surface temperature of 135°C and rolling compression was performed and subsequently drawing was further performed to 7 times.

The compression molding sheet produced was then slitted to form a width of 30 mm to form a tape, and drawing was performed using a drawing device with the specification

shown below. Drawing was performed three times under the conditions shown in Table I and a material with a total drawing ratio of 63 times was produced.

Specifications of drawing device

1. Heating medium

3 rolls of pre-heating metal: roll diameter of 250 mm and length of 200 mm

1 drawing metal roll: diameter 125 mm and length of 200 mm

Heating medium oil was circulated inside the roll

Roll distance of 30 mm in all cases

2. 3 cooling metal rolls: diameter 250 mm, length 200 mm

Water was circulated inside the roll

3. Nip roll

Entrance side: 200 mm silicone rubber roll is used as a nip roll for two metal rolls used for pre-heat treatment

Exit side: 200 mm silicone rubber roll is used as a nip roll for two metal rolls used for cooling.

Table I

	Metal roll temperature (°C)		Nip roll tangential speed (m/min)		Drawing ratio (times)
	Pre-heating	Drawing	Entrance side	Exit side	
First time	135	140	1	3	3
Second time	140	145	4	8	2
Third time	140	145	10	15	1.5
Total					9

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The above-mentioned polyethylene drawn material was cut to form a length of 500 mm, a weight was applied to the material and dipped inside a 300 ml beaker filled with 200 ml of water. 100 ml water was filled in an ultrasonic wave generator (oscillation frequency and output are 40 kHz and 55 W, respectively) and the above-mentioned beaker was placed and an ultrasonic treatment was performed at a temperature of 25°C for 30 min.

In this manner, a polyolefin material with a fibril structure having a fibril with a diameter of approximately 1 ~ 15 μm in the same direction was produced. A part of the polyolefin material with a fibril structure produced as described above was cut, and the electron microscope image produced is shown in Fig. 3. In this case, the magnification ratio of the above-mentioned image is 200 times.

<u>Application Example 2</u>

A compression molding was performed for an ultra-high molecular weight polyethylene powder having an ultimate viscosity in a 135°C decaline of 16.7 dl/g and melting point of 143°C by a press machine under a pressure of approximately 100 kgf/cm^2, and at a temperature of 130°C so as to produce a sheet having a thickness of 1.0 mm and a length of 100 mm.

Then, the above-mentioned sheet was supplied to between a pair of rolls having a roll distance of 50 μm and roll surface temperature of 135°C, rolling compression was performed and drawing was performed to form a length of 7 times.

A sample piece measuring a width of 50 mm and a length of 100 mm was cut out from the above-mentioned rolled sheet, stretching was performed under tension by a tensile tester equipped with a temperature controlled tank at a temperature of 135°C and pulling

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speed of 50 mm/min to form a length of 6 times the original length and the total stretching ratio of the rolling compression and drawing of 42 times was achieved so as to produce a drawn polyethylene material having a width of 15 mm and a length of 110 μm.

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The above-mentioned polyethylene drawn material was cut to 300 mm, and an ultrasonic treatment was performed as in the case of Application Example 1 using an ultrasonic wave generator having an oscillation frequency and output of 100 kHz and 75 W, respectively, and ultrasonic treatment of 20 min. As a result, a fibrilous drawn material was produced as in the case of Application Example 1. In this case, the above-mentioned material had a fibril having a diameter of approximately $0.5 \sim 10$ μm in the same direction.

Comparative Example 1

In Application Example 1, the ultrasonic treatment was omitted, and a treatment was performed in the same manner. The electron microscope image of the drawn polyethylene material produced is shown in Fig. 4. In this case, the magnification ratio of the above-mentioned image is 200 times.

Measurement method used for melting point:

5 mg of the sample was set for the DSC device and a measurement was performed under conditions of a temperature increase rate of 5°C/min and the absorption peak temperature obtained was defined as the melting point.

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4. Brief description of figures

Fig. 1 and fig. 2 are examples of the compression molding device effectively used in the present invention, Fig. 3 is the scanning electron microscope image of the polyolefin material with a fibril structure produced by the method of the present invention and Fig. 4 is the scanning electron microscope image of the polyolefin material with a fibril structure produced by a conventional method.

[Definition of codes]

1 ~ 4: Rolls

5,6: Endless belt

7: Pressure plate

8: Group of rollers

9: Chain

10: Sprocket

11: Heating unit

12: Pre-heating unit

13: Insulation member

14: Hopper

15: Hydraulic piston

Applicant: Japan Petroleum Corp.

Agent: Tadashi Wakabayashi, patent attorney

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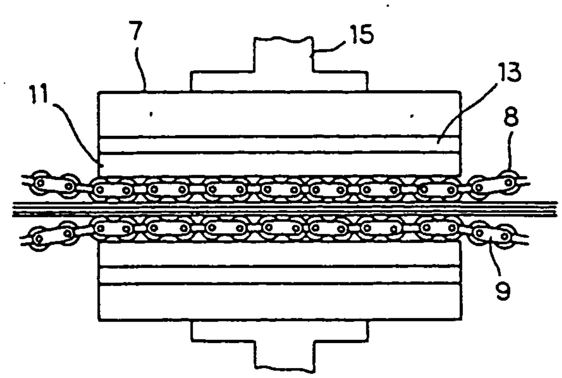
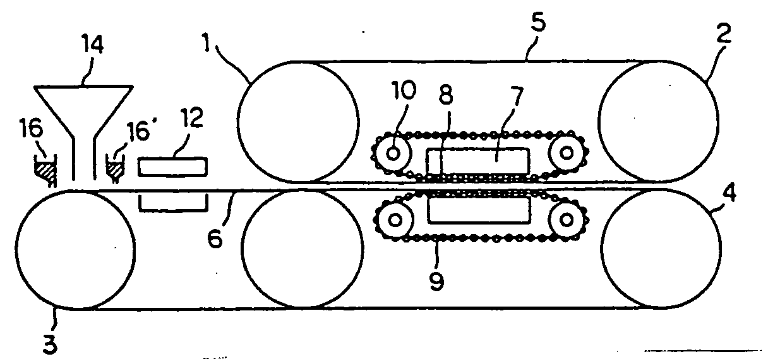
[Fig. ~~1~~]



1
[Fig. ~~2~~]



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